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THE

PHYSICAL REVIEW

A NOTE ON THE SPECTRA OF DOUBLY AND TREBLY IONIZED LEAD

By Stanley Smith
University of Alberta

(Received May 27, 1930)

Abstract

In the spectrum of Pb III three new singlet terms *viz.* $6s7s\,^1S_0$, $6s7p\,^1P_1$ and $6s7d\,^1D_2$ have been found to give rise to seventeen new lines which are here reported.

Certain discrepancies between the classification of terms by A. S. Rao and A. L. Narayan and the writer are discussed.

In the spectrum of Pb IV the previously published classifications of lines by J. A. Carroll, A. S. Rao and A. L. Narayan are discussed, and certain anomalies are pointed out. Two schemes different in some respects from those already put forward are suggested.

Spectrum of Pb III

THE spectrum of Pb III has been discussed in several papers[1,2,3] published during the past two years. The investigation of this spectrum has been continued by the writer and has led to the identification of three more singlet terms, which have been classified as $6s7s\,^1S_0$, $6s7p\,^1P_1$ and $6s7d\,^1D_2$. In the meanwhile a further paper by A. S. Rao and A. L. Narayan[4] has appeared in which there is agreement with the writer with regard to the $6s7p\,^1P_1$ term but disagreement as to the identity of the term classified by the writer as $6s7s\,^1S_0$. As there are also further discrepancies between the results it was thought that it would be of interest to discuss these and to bring the information with regard to this spectrum up to date by adding a list of the new combinations which have been classified.

The data used in this investigation are the vacuum spark measurements of Mack,[5] of R. J. Lang (unpublished) and of the writer.[6] Spectrograms of the Schüler lamp discharge in the region from 1900A to 7000A obtained by the writer have also been found to be useful in this work. The writer is also

[1] K. R. Rao, A. L. Narayan and A. S. Rao. Indian Journ. Phys. **2**, 467 (1928).
[2] S. Smith, Proc. Nat. Acad. Sci. **14**, 878 (1928).
[3] S. Smith, Phys. Rev. **34**, 393 (1929).
[4] A. S. Rao and A. L. Narayan, Zeits. f. Physik **59**, 687 (1930).
[5] J. E. Mack, Phys. Rev. **34**, 17 (1929).
[6] S. Smith, Trans. Roy. Soc. Canada **22**, 331 (1928).

indebted to Dr. Lang for a plate of this spectrum taken on his vacuum spectrograph in the region 1300A to 2200A.

The two main points of disagreement between the classification of Rao and Narayan and that of the writer are in connection with the $6s7d\,^3D_{1,2,3}$ and $6s6d\,^1D_2$ terms. With regard to the $6s7d\,^3D_{1,2,3}$ terms Rao's choice does not lead to any observed lines in the predicted positions for the $6s6p\,^3P_{0,1,2} - 6s7d\,^3D_{1,2,3}$ combinations, whereas the terms selected by the writer do give fairly close agreement between predicted and observed lines for these combinations. Moreover the observed lines λλ4094, 4128, which apparently arise from combinations between $6s7d\,^3D_{1,2}$ and the newly found term $6s7p\,^1P_1$, may be considered as further evidence in support of the validity of the writer's choice of the $6s7d\,^3D_{1,2,3}$ terms. Turning now to the term $\nu = 104998$, classified by Rao as $6s6d\,^1D_2$ and by the writer as $6s7s\,^1S_0$, it will be noted that Rao gives λλ4272, 4496 as the combinations between this term and $6s7p\,^1P_1$ and $6s7p\,^3P_2$ respectively. If this classification is correct then the inner quantum number of the term in question clearly cannot be 0. However it is found that the wave-number difference between λλ4272, 4496 is 1163.6 whereas the value of $6s7p\,^3P_2 - 6s7p\,^1P_1$, deduced from the appropriate combinations using measurements in a region where the wave-lengths are known to a fairly high degree of accuracy, is 1158.4. This is so large a discrepancy that it throws doubt on the above mentioned classification of λλ4272, 4496. It is possible that λ4496 is a $6s6d\,^3D$ combination as this line differs in wave-number from the line λ4400, which also appears to be a line of doubly ionized lead, by 481.6. This is the value of the $6s6d\,^3D_{1,2}$ separation. The $6s6d\,^1D_2$ term has been previously given by the writer and λ3951 appears to be the combination between this term and the newly found $6s7p\,^1P_1$ term and not an *FG* combination as classified by Rao. The lines λλ2948, 3451, given by Rao as $6s7p\,^3P_{1,2} - 6p7p\,^3P_2$ appear with considerable intensity on the Schüler lamp plates and are therefore to be attributed to Pb II.

The lines involving the new terms are given in Table I.

TABLE I. *New classified lines of Pb III.*

λI.A. air	Int.	ν	Classification		
5780.0	3	17296	$6s7s\,^1S_0 - 6s7p\,^3P_1$		
*5191.9	3	19255	$6s6d\,^3D_2 - 6s7p\,^1P_1$		
*5064.4	1	19740	$6s6d\,^3D_1 - 6s7p\,^1P_1$		
4855.14	2	20591.0	$6p6p\,^3P_1 - 6s7p\,^3P_2$		
*4827.02	3	20710.9	$6s7p\,^1P_1 - 6s8s\,^3S_1$	Term	Value
4596.53	1	21749.5	$6s6p\,^3P_1 - 6s7p\,^1P_1$	$6s7s\,^1S_0$	104998
4499.51	6	22218.4	$6s7p\,^1P_1 - 6s7d\,^1D_2$	$6s7p\,^1P_1$	81600
4272.63	5	23398.2	$6s7s\,^1S_0 - 6s7p\,^1P_1$	$6s7d\,^1D_2$	59382
4128.21	2	24216.8	$6s7p\,^1P_1 - 6s7d\,^3D_1$		
4094.68	3	24415.1	$6s7p\,^1P_0 - 6s7d\,^3D_2$		
3951.94	7	25296.9	$6s6d\,^1D_2 - 6s7p\,^1P_1$		
*3689.32	5	27097.6	$6s7s\,^3S_1 - 6s7p\,^1P_1$		
3530.35	1	28317.7	$6s7p\,^3P_1 - 6s7d\,^1D_2$		
λI.A. vac.					
1711.23	4	58437	$6s6p\,^1P_1 - 6s7s\,^1S_0$		
1118.67	4	89392	$6s6p\,^3P_1 - 6s7s\,^1S_0$		
1070.83	0	93385	$6s6p\,^3P_0 - 6s7s\,^1S_0$ (?)		
961.01	1	104057	$6s6p\,^1P_1 - 6s7d\,^1D_2$		

* Given by Rao and Narayan.

Spectrum of Pb IV

The first investigation of this spectrum was made by Carroll,[7] who gave the $6s\,^2S_1-6p\,^2P_{1,2}$ doublet, two of the $6d\,^2D_{2,3}-5f\,^2F_{3,4}$ triplet, and two choices for the $6p\,^2P_{1,2}-6d\,^2D_{2,3}$ triplet, the first of which included the line λ1069, which has since been shown to be a Pb III line. An extension of this spectrum based on Carroll's identifications has recently been published by Rao and Narayan,[8] but their classification does not appear to be a very probable one. The lines λλ3909, 3279, 3089, selected in Rao's scheme have been found to belong to Pb III. λλ1726, 1796 chosen by Carroll and by Rao as two of the $6d\,^2D_{2,3}-5f\,^2F_{3,4}$ triplet are found as very strong lines on the Schüler lamp spectrogram and therefore, in all probability, are to be attributed to Pb II. The writer has attempted to make a more probable selection, and a tentative scheme based on Carroll's second choice for the diffuse triplet is presented in Table II.

Table II. *Classified lines of Pb IV.*

λ I.A.	Int.	ν	$\Delta\nu$	Classification
*1028.61	15	97218		$6s\,^2S_1-6p\,^2P_2$
			21063	
*1313.12	15	76155		$6s\,^2S_1-6p\,^2P_1$
*922.53	4	108398		$6p\,^2P_1-6d\,^2D_2$
			21057	
*1116.10	5	89598		$6p\,^2P_2-6d\,^2D_3$
			2257	
*1144.94	5	87341		$6p\,^2P_2-6d\,^2D_2$
3002.78	2	33292.8		$6d\,^2D_2-7p\,^2P_1$
			2258.4	
3221.30	6	31034.4		$6d\,^2D_3-7p\,^2P_2$
			8063.0	
3962.45	6	25229.8		$6d\,^2D_2-7p\,^2P_1$
3052.66	7	32748.8		$7s\,^2S_1-7p\,^2P_2$
			8063.1	
4049.79	4	24685.7		$7s\,^2S_1-7p\,^2P_1$
2508.98	2	39844.8		$7p\,^2P_1-7d\,^2D_2$
			8063.5	
3087.10	4	32383.5		$7p\,^2P_2-7d\,^2D_3$
			602.2	
3145.60	2	31781.3		$7p\,^2P_2-7d\,^2D_2$

* Selected by Carroll.

An alternative classification of the triplets involving $6d\,^2D_{2,3}$ terms in which these terms are inverted, as in the case of the doublet D terms of Pb II,[9] is given in Table III. In these tables the wave-lengths are expressed in I.A.$_{air}$ above 2000A and in I.A.$_{vac}$ below 2000A. Mack's measures are used for the $6P-6D$ triplet in Table III.

[7] J. A. Carroll, Trans. Roy. Soc. **A225**, 357 (1925).
[8] A. S. Rao and A. L. Narayan, Zeits. f. Physik **61**, 149 (1930).
[9] H. Gieseler, Zeits. f. Physik **42**, 265 (1927).

TABLE III. *Alternative classification of lines of Pb IV.*

λI.A.	Int.	ν	Δν	Classification
*890.78	5	112261		$6p\,^3P_1-6d\,^3D_2$
			21059	
1096.47	2	91202		$6p\,^3P_2-6d\,^3D_2$
			−1604	
*1116.09	7	89598		$6p\,^3P_2-6d\,^3D_3$
2864.54	7	34899.4		$6d\,^3D_3-7p\,^3P_2$
			−1606.6	
3002.78	2	33292.8		$6d\,^3D_2-7p\,^3P_2$
3962.45	6	25229.8	8063.0	$6d\,^3D_2-7p\,^3P_1$

* Selected by Carroll in his first choice of the diffuse triplet.

The fundamental triplet has not been found in either scheme and the $7p\,^3P_{1,2}$ separation is larger than might be expected.

In conclusion I wish gratefully to acknowledge a grant from the National Research Council of Canada, which has been of assistance in this work.

THE SPARK SPECTRUM OF COBALT, Co II

By J. H. Findlay
Palmer Physical Laboratory, Princeton University

(Received May 19, 1930)

Abstract

A further examination of the Co II spectrum, based on the previous work of Meggers, has been made. A magnetic analysis shows that Meggers' classification of the terms now called $d^7p\ {}^5F^\circ$, ${}^5D^\circ$ should be interchanged, except for the term ${}^5F_4^\circ$. Since Meggers' results were obtained from intensity rules, the author's ${}^5F\ {}^5F^\circ$ and ${}^5F\ {}^5D^\circ$ multiplets show irregular intensities. The strongest lines in these multiplets are, respectively, ${}^5F_n\ {}^5F^\circ_{n-1}$ and ${}^5F_n\ {}^5D^\circ_n$. The magnetic analysis also shows that Meggers' terms ${}^3D$ should be $d^7s\ {}^5P$ and that his ${}^3P$, ${}^3D^1$, and ${}^3F$ should be partly $d^7p\ {}^5P^\circ$ and ${}^5D^\circ$. In addition, the terms $d^7s\ {}^3F$, $d^7p\ {}^5D^\circ$, ${}^3F^\circ$, ${}^3G^\circ$, ${}^5S^\circ$, ${}^5P^\circ$, ${}^5D^\circ$, and the lowest terms $d^8\ {}^3F$ have been found. The location of the second member of the $d^7s\ {}^5F\ {}^3F$ series gives an I. P. of 16.9 volts from d^7s to d^7 and 17.3 volts from d^8 to d^7, in practically exact agreement with the predictions of Dr. H. N. Russell.

Introductory Review

A PREVIOUS analysis of the first spark spectrum of cobalt was made by Meggers.[1] The purpose of the author's work was to extend Meggers' analysis with the aid of the Zeeman effect. The magnetic analysis afforded a change in the interpretation of several of Meggers' levels, and several new levels were found by the usual method of wave-number differences.

Experimental Procedure

The author was fortunate in having the use of unpublished measurements and intensity estimates in the region from λ5000 to λ2000 made by Dr. Meggers of the Bureau of Standards. Further measurements were also made by the author of sharp lines in the range from λ2000 to λ1940 and of diffuse lines from λ3000 to λ2550, the standards being the copper arc and spark lines calculated by Shenstone.[2] Meggers' measurements were corrected to agree with these standards.

A Hilger E1 quartz spectrograph was used with Cramer Contrast and Hilger Schumann plates in taking photographs for wave-length determinations, sheets of very pure cobalt serving as electrodes.

Zeeman effect photographs were taken from λ3700 to λ2190 with the same instrument and an electromagnet, giving a field of about 35,500 gauss with pole pieces 1 cm in diameter and an air gap of about 3 mm. A button of cobalt about 1 mm thick clamped against one of the pole pieces of the magnet served as the anode, and a copper rod with a small tip on the end bent at right angles to the rest of the rod was used as the cathode of an arc, carrying a current of about 1 ampere at 250 volts, in taking most of the

[1] W. F. Meggers, Journ. Wash. Ac. Sci. **18**, 325 (1928).
[2] A. G. Shenstone, Phys. Rev. **28**, 449 (1926); **29**, 380 (1927).

TABLE I. *Term table for Co II.*

Configuration	Designation: Author's	Designation: Meggers'	Level	g: Obs.	g: Landé	Intervals (Higher J's first)
$3d^8$	a^3F_4		0.0[b]			
$3d^8$	a^3F_3		950.3[b]			
$3d^8$	a^3F_2		1597.2[b]			
$3d^7(^4F)4s$	$4s^5F_5$	$^5F_5'$	3350.5 *	1.39	1.40	
"	$4s^5F_4$	$^5F_4'$	4028.9 *	1.36	1.35	
"	$4s^5F_3$	$^5F_3'$	4560.8 *	1.25	1.25	
"	$4s^5F_2$	$^5F_2'$	4950.0 *	1.00	1.00	
"	$4s^5F_1$	$^5F_1'$	5204.5 *	.00	.00	
"	$4s^3F_4$		9812.7*	1.28	1.25	
"	$4s^3F_3$		10708.1*	1.10	1.08	
"	$4s^3F_2$		11321.5*	0.60	0.67	
$3d^7(^4P)4s$	$4s^5P_3$	$^3D_3$	17771.5 *	1.70	1.67	
"	$4s^5P_2$	$^3D_2$	18031.5 *	1.86	1.83	
"	$4s^5P_1$	$^3D_1$	18338.5 *	2.48	2.50	
$3d^7(^4F)4p$	$4p^5F_5^\circ$	$^5F_5$	45197.8*	1.40	1.40	
"	$4p^5F_4^\circ$	$^5D_4'$	45378.8*	1.38	1.35	
"	$4p^5F_3^\circ$	$^5D_3'$	45972.1*	1.26	1.25	
"	$4pz^5D_4^\circ$	$^5F_4$	46320.8 *	1.48	1.50	
"	$4p^5F_2^\circ$	$^5D_2'$	46452.6*	1.02	1.00	
"	$4p^5F_1^\circ$	$^5D_1'$	46786.3*	.00	.00	
"	$4pz^5D_3^\circ$	$^5F_3$	47039.0 *	1.51	1.50	
"	$4p^5G_6^\circ$	$^5G_6'$	47078.2 *	1.33	1.33	
"	$4p^5G_5^\circ$	$^5G_5'$	47345.7 *	1.27	1.27	
"	$4pz^5D_2^\circ$	$^5F_2$	47537.1 *	1.52	1.50	
"	$4p^5G_4^\circ$	$^5G_4'$	47807.2 *	1.15	1.15	
"	$4pz^5D_1^\circ$	$^5F_1$	47848.5 *	1.53	1.50	
"	$4pz^5D_0^\circ$		47995.1 *	0/0	0/0	
"	$4p^5G_3^\circ$	$^5G_3'$	48150.7 *	0.92	0.92	
"	$4p^5G_2^\circ$	$^5G_2'$	48388.1 *	0.33	0.33	
"	$4p^3G_5^\circ$		48555.9*	1.20	1.20	
"	$4p^3G_4^\circ$		49348.2*	1.09	1.05	
"	$4p^3F_4^\circ$		49697.5 *	1.20	1.25	
"	$4p^3G_3^\circ$		50035.9*	0.80	0.75	
"	$4p^3F_3^\circ$		50381.6 *	1.08	1.08	
"	$4p^3F_2^\circ$		50913.8 *	0.65	0.67	
"	$4p^3D_3^\circ$		51512.2*	1.32	1.33	
"	$4p^3D_2^\circ$		52229.6*	1.16	1.17	
"	$4p^3D_1^\circ$		52684.5*	0.45	0.50	
$3d^7(^4P)4p$	$4p^5S_2^\circ$		56010.6	1.99	2.00	
"	$4py^5D_3^\circ$	$^3D_3'$	61240.8 *	1.51	1.50	
"	$4py^5D_2^\circ$	$^3D_2'$	61260.1 *	1.51	1.50	
"	$4py^5D_1^\circ$		61348.5 *(?)	—	1.50	
"	$4py^5D_4^\circ$		61388.1 *	1.50	1.50	
"	$4py^5D_0^\circ$		61457.9 *	0/0	0/0	
"	$4p^5P_3^\circ$	$^3P_2$	63344.1*	1.67	1.67	
"	$4p^5P_2^\circ$	$^3F_2$	63366.9*	1.86	1.83	
"	$4p^3P_2^\circ$		63615.7	1.33	1.50	
"	$4p^5P_1^\circ$	$^3P_1$	63665.0*	2.62	2.50	
$3d^7(^4F)5s$	$5s^5F_5$		84012.3 *			
"	$5s^5F_4$		84584.8 *			
"	$5s^5F_3$		85165.3 *			
"	$5s^3F_4$		85479.2*			
"	$5s^5F_2$		85593.9 *			
"	$5s^5F_1$		85874.1 *			
"	$5s^3F_3$		86343.8*			
"	$5s^3F_2$		86937.7*			

a^3F 950.3, 646.9
$4s^5F$ 678.4, 531.9, 389.2, 254.5
$4s^3F$ 895.4, 613.4
$4s^5P$ 260, 307
$4p^5F^\circ$ 181.0, 593.3, 480.5, 333.7
$4p_z{}^5D^\circ$ 718.2, 498.1, 311.4, 146.6
$4p^5G^\circ$ 267.5, 461.5, 343.5, 237.4
$4p^3G^\circ$ 792.3, 687.3
$4p^3F^\circ$ 684.1, 532.2
$4p^3D^\circ$ 717.4, 454.9
$4py^5D^\circ$ −147.3, 19.3, 88.4, 109.4
$4p^5P^\circ$ 22.8, 298.1
$5s^5F$ 572.5, 580.5, 428.6, 280.2
$5s^3F$ 864.6, 593.9

Zeeman effect photographs, the exposures of which were fron 5 to 15 minutes. A blast of nitrogen blowing over the arc kept the cobalt from burning away too rapidly and, hence, made the arc run more steadily. Under these conditions, most of the lines appearing on the Zeeman effect plates were cobalt spark lines. However, in the region from λ3700 to λ3000 a spark discharge had to be used as a light source to bring out the spark lines. A few copper lines appeared on the plates. Of these λ3273.97 ($^2S_{\frac{1}{2}}-{}^2P_{\frac{1}{2}}$), λ2441.63 ($^2S_{\frac{1}{2}}-{}^4P_{\frac{1}{2}}$), and λ2181.71 ($^2S_{\frac{1}{2}}-{}^2P_{\frac{1}{2}}$) were used to determine the field. A quartz double image prism separated the parallel and perpendicular components of the patterns.

Term Designation

The Hund theory predicts that the low terms should be ^3F from the structure $3d^8$, and $^{3\&5}F$, $^{3\&5}P$, etc. from the structure $3d^74s$. The middle terms shoud be the $^{3\&5}S^0$, P^0, D^0, F^0, G^0, etc. from $3d^74p$. Many of these terms have been discovered and are given in Table I together with the $^{3\&5}F$ from $3d^75s$. The notation used is that recommended by H. N. Russell, A. G. Shenstone, and L. A. Turner.[3]

Table II. *Resolved Zeeman patterns of Co II.*

λ	$X-Y$	Z.E. Pattern	Remarks
3370.94	$4s^5P_1-4pz^5D_0^\circ$	O(0.00) 2.40 C(0.00) 2.50	Good measurements not expected in this range.
2524.98	$4s^3F_2-4p^3F_2^\circ$	O(0.00) 0.68 C(0.00) 0.67	
2423.61	$4s^5F_1-4p^5F_2^\circ$	O(0.00, 1.10) 0.00, 1.10, 2.20 C(0.00, 1.00) 0.00, 1.00, 2.00	Discrepancy here unexplained.
2417.66	$4s^5F_4-4p^5F_4^\circ$	O(0.00) 1.39 C(0.00) 1.35	
2414.06	$4s^5F_3-4p^5F_3^\circ$	O(0.00) 1.26 C(0.00) 1.25	
2408.76	$4s^5F_2-4p^5F_2^\circ$	O(0.00) 1.01 C(0.00) 1.00	
2404.17	$4s^5F_1-4p^5F_1^\circ$	O(0.00) 0.00 C(0.00) 0.00	
2389.54	$4s^5F_2-4p^5F_1^\circ$	O(0.00, 0.92) 0.00, 0.92, 2.00 C(0.00, 1.00) 0.00, 1.00, 2.00	Discrepancy also unexplained.
2388.90	$4s^5F_5-4p^5F_5^\circ$	O(0.00) 1.39 C(0.00) 1.40	
2361.52	$4s^5F_1-4pz^5D_2^\circ$	O(0.00, 1.50) 0.00, 1.50, 3.00 C(0.00, 1.50) 0.00, 1.50, 3.00	
2344.26	$4s^5F_1-4pz^5D_1^\circ$	O(1.52), 0.00, 1.53 C(1.50), 0.00, 1.50	
2336.23	$4s^5F_1-4pz^5D_0^\circ$	O(0.00) 0.00 C(0.00) 0.00	
2318.41	$4s^5P_1-4py^5D_0^\circ$	O(0.00) 2.48 C(0.00) 2.50	
2220.11	$4s^5P_1-4p^5P_2^\circ$	O(0.00, 0.88) 0.92, 1.86, faint. C(0.00, 0.67) 1.17, 1.83, 2.50	
2207.90	$4s^5P_1-4p^3P_2^\circ$	O(0.00, 1.18) 0.00, 1.33, faint. C(0.00, 1.00) 0.50, 1.50, 2.50	Unsymmetrical in π and σ. 0.50 components in σ unresolved.

[3] H. N. Russell, A. G. Shenstone, L. A. Turner, Phys. Rev. **33**, 900 (1929).

Zeeman Effect

Several resolved patterns were obtained on the Zeeman effect photographs. Table II gives both the observed and calculated arrangement of these patterns. However, most of the lines appeared as simple triplets due to the low resolving power of the instrument. Nevertheless, a formula described by Shenstone and Blair[4] allowed the calculation of g-values from the unresolved patterns. The g's calculated from all the resolved and unresolved patterns are consistent with the assumption that all the terms have Landé g-values.

The magnetic analysis readily indicated that Meggers' classification of the ^5F and $^5D'$ terms should be interchanged except for $^5F_5$, his ^3D terms should be $4s^5P$, and his ^3P, $^3D'$, and ^3F should be partly $d^7p^5P^0$ and $^5D^0$.

Since Meggers' results were based on intensity rules, the author's $4s^5F4p^5F^0$ and $4s^5F4p^5D^0$ multiplets show the irregular intensities indicated in Table III. In the case of spectra in which the Russell-Saunders coupling is broken down, there are usually irregular intensities, the g-values depart from Landé values, and the interval rule is not obeyed. In this spectrum, however, the interval rule is obeyed fairly well, and the terms have Landé g-values, yet two of the three principal multiplets show very anomalous intensities.

Table III. *Intensities in the principal multiplets.*

	$4s^5F_5$	$^5F_4$	$^5F_3$	$^5F_2$	$^5F_1$
$4p_z{}^5D_4^\circ$	25	80	10		
$^5D_3^\circ$		40	60	15	
$^5D_2^\circ$			30	30	10
$^5D_1^\circ$				30	25
$^5D_0^\circ$					20
$^5F_5^\circ$	100	10			
$^5F_4^\circ$	100	40	10		
$^5F_3^\circ$		80	40	10	
$^5F_2^\circ$			50	25	10
$^5F_1^\circ$				40	20
$^5G_6^\circ$	100				
$^5G_5^\circ$	8	75			
$^5G_4^\circ$	2	15	50		
$^5G_3^\circ$		3	20	40	
$^5G_2^\circ$			4	15	30

Ionization Potentials

The limits of the $4s^5F$, ^3F series were determined by the application of a Rydberg formula to the two members of these series. However, on account of the inaccuracy of a Rydberg formula, this calculation did not, as is to be expected, give any indication of the four separate limits approached by the eight series.

The limit of the $4s^5F_5$ series gives an ionization potential of 16.9 volts from $3d^74s$ to $3d^7$, and 17.3 volts from $3d^8$ to $3d^7$. Using H. N. Russell's[5]

[4] A. G. Shenstone and H. A. Blair, Phil. Mag. **8**, 765 (1929).

[5] H. N. Russell, Astrophys. J. **66**, 223 (1927).

TABLE IV. *Classified lines of Co II.*

λ(Air)	Int.	Auth.	ν(Vac.)	Combination
3621.22	100	M	27607.2	$4s^5P_3-4p^5F_4^\circ$
3578.03	30	M	27940.5	$4s^5P_2-4p^5F_3^\circ$
3555.93	10	M	28114.0	$4s^5P_1-4p^5F_2^\circ$
3545.03	25	M	28200.5	$4s^5P_2-4p^5F_2^\circ$
3517.48	10	M	28421.3	$4s^5P_2-4p^5F_3^\circ$
3514.21	5	M	28447.8	$4s^5P_1-4p^5F_1^\circ$
3501.73	200	M	28549.2	$4s^5P_3-4pz^5D_4^\circ$
3446.40	100	M	29007.5	$4s^5P_3-4pz^5D_3^\circ$
3423.85	75	M	29198.6	$4s^5P_1-4pz^5D_2^\circ$
3415.78	75	M	29267.5	$4s^5P_3-4pz^5D_3^\circ$
3388.18	50	M	29505.8	$4s^5P_2-4pz^5D_2^\circ$
3387.72	60	M	29509.9	$4s^5P_1-4pz^5D_1^\circ$
3370.94	50	M	29656.8	$4s^5P_1-4pz^5D_0^\circ$
3358.59	10	M	29765.9	$4s^5P_2-4pz^5D_2^\circ$
3352.80	30	M	29817.3	$4s^5P_2-4pz^5D_1^\circ$
2943.16	30u	M	33967.2	$4p^3D_3^\circ-5s^3F_4$
2930.45	10u	M	34114.5	$4p^3D_2^\circ-5s^3F_3$
2883.43	1	F	34670.7	$4s^3F_3-4p^5F_4^\circ$
2880.32	3u	F	34708.2	$4p^3D_2^\circ-5s^3F_2$
2870.03	3u	F	34832.7	$4p^3D_3^\circ-5s^3F_3$
2848.36	5u	F	35097.6	$4p^3F_3^\circ-5s^3F_4$
2845.64	2	F	35131.0	$4s^3F_2-4p^5F_2^\circ$
2834.92	2	M	35264.0	$4s^3F_3-4p^5F_3^\circ$
2825.22	8	M	35385.1	$4s^3F_4-4p^5F_5^\circ$
2821.63	5u	F	35430.1	$4p^3F_2^\circ-5s^3F_3$
2818.86	1	M	35464.9	$4s^3F_2-4p^5F_1^\circ$
2810.85	5	M	35566.0	$4s^3F_4-4p^5F_4^\circ$
2807.17	2	M	35612.6	$4s^3F_3-4pz^5D_4^\circ$
2798.92	2	F	35717.5	$4s^3F_3-4pz^5D_3^\circ$
2796.86	2	F	35744.8	$4s^3F_2-4p^5F_2^\circ$
2793.93	20u	F	35781.3	$4p^3F_4^\circ-5s^3F_4$
2779.82	20u	F	35962.9	$4p^3F_3^\circ-5s^3F_3$
2775.11	20u	F	36024.0	$4p^3F_2^\circ-5s^3F_2$
2766.85	30u	F	36131.6	$4p^3G_4^\circ-5s^3F_4$
2764.75	1	F	36159.1	$4s^3F_4-4p^5F_3^\circ$
2753.38	10u	F	36308.2	$4p^3G_3^\circ-5s^3F_3$
2738.32	1	F	36508.1	$4s^3F_4-4pz^5D_4^\circ$
2736.91	2	M	36526.8	$4s^3F_2-4pz^5D_1^\circ$
2734.68	10u	F	36556.6	$4p^3F_3^\circ-5s^3F_3$
2727.91	20u	F	36647.3	$4p^3F_4^\circ-5s^3F_4$
2714.40	15	M	36829.7	$\begin{cases}4s^3F_3-4p^5G_3^\circ\\4s^3F_3-4pz^5D_2^\circ\end{cases}$
2709.12	10u	F	36901.4	$4p^3G_3^\circ-5s^3F_3$
2707.55	30u	F	36922.8	$4p^3G_4^\circ-5s^3F_4$
2706.72	50u	F	36934.2	$4p^3G_5^\circ-5s^3F_5$
2702.19	20u	F	36996.0	$4p^3G_4^\circ-5s^3F_3$
2697.02	3	M	37067.0	$4s^3F_3-4p^5G_3^\circ$
2694.65	25	M	37099.6	$4s^3F_3-4p^5G_4^\circ$
2686.97	1u	F	37205.6	$4p^5G_3^\circ-5s^5F_2$
2684.50	50u	F	37239.8	$4p^5G_5^\circ-5s^5F_4$
2676.03	20u	F	37357.7	$4p^5G_4^\circ-5s^5F_3$
2669.89	10u	F	37443.6	$4p^5G_3^\circ-5s^5F_2$
2666.82	5u	F	37486.7	$4p^5G_2^\circ-5s^5F_1$
2663.52	60	M	37533.2	$4s^3F_4-4p^5G_5^\circ$
2662.64	2u	F	37545.6	$4pz^5D_3^\circ-5s^5F_4$
2653.68	15	M	37672.3	$4s^5P_1-4p^5S_2^\circ$
2653.16	1	F	37679.6	$4s^3F_3-4p^5G_2^\circ$
2652.36	5u	F	37691.1	$4pz^5D_4^\circ-5s^5F_5$
2639.26	2u	F	37878.1	$4pz^5D_0^\circ-5s^5F_1$
2632.22	30	M	37979.4	$4s^5P_2-4p^5S_2^\circ$
2629.01	0u	F	38025.7	$4pz^5D_1^\circ-5s^5F_1$
2626.89	10u	F	38056.4	$4pz^5D_2^\circ-5s^5F_2$
2622.06	5u	F	38126.5	$4pz^5D_3^\circ-5s^5F_3$

TABLE IV. *Continued.*

λ(Air)	Int.	Auth.	ν(Vac.)	Combination
2614.37	20	M	38238.7	$4s^5P_3-4p^5S_2^\circ$
2612.63	10u	F	38264.1	$4pz^5D_4^\circ-5s^5F_4$
2592.90	2u	F	38555.3	$4pz^5D_3^\circ-5s^5F_2$
2582.37	4u	F	38612.5	$4p^5F_3^\circ-5s^5F_4$
2580.93	5u	F	38634.0	$4p^5F_4^\circ-5s^5F_5$
2587.23	60	M	38639.8	$4s^3F_3-4p^3G_4^\circ$
2582.27	50	M	38714.0	$4s^3F_2-4p^3G_3^\circ$
2580.35	100	M	38742.8	$4s^3F_4-4p^3G_5^\circ$
2575.61	5u	F	38814.1	$4p^5F_5^\circ-5s^5F_5$
2564.04	75	M	38989.3	$4s^3F_3-4p^3F_4^\circ$
2559.41	40	M	39059.8	$4s^3F_2-4p^3F_3^\circ$
2554.09	2u	F	39141.1	$4p^5F_2^\circ-5s^5F_2$
2550.69	5u	F	39193.3	$4p^5F_3^\circ-5s^5F_3$
2549.90	5u	F	39205.4	$4p^5F_4^\circ-5s^5F_4$
2541.95	50	M	39328.1	$4s^3F_3-4p^3G_3^\circ$
2528.61	50	M	39535.5	$4s^3F_4-4p^3G_4^\circ$
2524.98	80	M	39592.4	$4s^3F_2-4p^3F_2^\circ$
2519.82	60	M	39673.4	$4s^3F_3-4p^3F_3^\circ$
2506.47	70	M	39884.7	$4s^3F_4-4p^3F_4^\circ$
2487.43	4	M	40190.0	$4s^3F_2-4p^3D_3^\circ$
2486.45	35	M	40205.8	$4s^3F_3-4p^3F_2^\circ$
2485.36	10	M	40223.5	$4s^3F_4-4p^3G_3^\circ$
2464.20	35	M	40568.8	$4s^3F_4-4p^3F_3^\circ$
2450.01	35	M	40803.8	$4s^3F_3-4p^3D_3^\circ$
2449.15	10	M	40818.1	$4s^5F_3-4p^5F_4^\circ$
2443.77	40	M	40908.0	$4s^3F_2-4p^3D_2^\circ$
2436.98	10	M	41021.9	$4s^5F_2-4p^5F_3^\circ$
2428.29	10	M	41168.7	$4s^5F_4-4p^5F_5^\circ$
2423.61	10	M	41248.2	$4s^5F_1-4p^5F_2^\circ$
2417.66	40	M	41349.7	$4s^5F_4-4p^5F_4^\circ$
2416.90	30	M	41362.7	$4s^3F_2-4p_3D_1^\circ$
2414.06	40	M	41411.4	$4s^5F_3-4p^5F_3^\circ$
2408.76	25	M	41502.5	$4s^5F_2-4p^5F_2^\circ$
2407.67	20	M	41521.3	$4s^3F_3-4p^3D_2^\circ$
2404.17	20	M	41581.7	$4s^5F_1-4p^5F_1^\circ$
2397.38	60	M	41699.5	$4s^3F_4-4p^3D_3^\circ$
2393.91	10	M	41759.9	$4s^5F_3-4pz^5D_4^\circ$
2389.54	40	M	41836.3	$4s^5F_2-4p^5F_1^\circ$
2388.90	100	M	41847.5	$4s^5F_5-4p^5F_5^\circ$
2386.37	50	M	41891.9	$4s^5F_3-4p^5F_2^\circ$
2383.45	80	M	41943.2	$4s^5F_4-4p^5F_3^\circ$
2378.62	100	M	42028.3	$4s^5F_5-4p^5F_4^\circ$
2375.19	15	M	42089.0	$4s^5F_2-4pz^5D_2^\circ$
2363.79	80	M	42292.0	$4s^5F_4-4pz^5D_4^\circ$
2361.53	10	M*	42332.5	$4s^5F_1-4pz^5D_2^\circ$
2353.43	60	M*	42478.0	$4s^5F_3-4pz^5D_3^\circ$
2347.41	30	M*	42587.1	$4s^5F_2-4pz^5D_2^\circ$
2344.26	25	M*	42644.0	$4s^5F_1-4pz^5D_1^\circ$
2336.24	20	M*	42790.6	$4s^5F_1-4pz^5D_0^\circ$
2330.37	30	M*	42898.5	$4s^5F_2-4pz^5D_1^\circ$
2329.12	10	M*	42921.4	$4s^5P_1-4py^5D_2^\circ$
2326.49	25	M*	42970.0	$4s^5F_5-4pz^5D_4^\circ$
2326.13	20	M*	42976.5	$4s^5F_3-4pz^5D_2^\circ$
2324.32	40	M*	43010.2	$4s^5F_4-4pz^5D_3^\circ$ $4s^5P_1-4py^5D_1^\circ$
2318.43	8	M*	43119.4	$4s^5P_1-4py^5D_0^\circ$
2314.99	30	M*	43183.5	$4s^5F_1-4p^5G_2^\circ$
2314.05	40	M*	43200.9	$4s^5F_2-4p^5G_3^\circ$
2313.60	8	M*	43209.4	$4s^5P_2-4py^5D_3^\circ$
2312.55	10	M*	43228.9	$4s^5P_2-4py^5D_2^\circ$
2311.62	50	M*	43246.5	$4s^5F_3-4p^5G_4^\circ$
2307.86	75	M*	43316.9	$4s^5P_2-4py^5D_1^\circ$ $4s^5F_4-4p^5G_5^\circ$

TABLE IV. *Continued.*

λ(Air)	Int.	Auth.	ν(Vac.)	Combination
2301.42	15	M*	43438.1	$4s^5F_2-4p^5G_2^\circ$
2299.77	25	M*	43469.1	$4s^5P_3-4py^5D_3^\circ$
2298.74	10	M*	43488.6	$4s^5P_3-4py^5D_2^\circ$
2293.41	30	M*	43589.8	$4s^5F_3-4p^5G_2^\circ$
2292.00	40	M*	43616.6	$4s^5P_3-4py^5D_4^\circ$
2286.17	150	M*	43727.7	$4s^5F_5-4p^5G_6^\circ$
2283.54	20	M*	43778.2	$4s^5F_4-4p^5G_4^\circ$
2280.98	4	M*	43827.3	$4s^5F_3-4p^5G_2^\circ$
2272.28	20	M*	43995.1	$4s^5F_5-4p^5G_5^\circ$
2265.76	6	M*	44121.6	$4s^5F_4-4p^5G_3^\circ$
2248.68	8	M*	44456.7	$4s^5F_5-4p^5G_4^\circ$
2245.13	100	M*	44527.0	$4s^5F_4-4p^3G_5^\circ$
2232.08	50	M*	44787.4	$4s^5F_3-4p^3G_4^\circ$
2220.14	15	M*	45028.3	$4s^5P_1-4p^5P_2^\circ$
2217.30	4	M*	45085.7	$4s^5F_2-4p^3G_3^\circ$
2214.80	20	M*	45136.6	$4s^5F_3-4p^3F_4^\circ$
2211.44	30	M*	45205.3	$4s^5F_5-4p^3G_5^\circ$
2207.93	50	M*	45277.1	$4s^5P_1-4p^3P_2^\circ$
2206.21	75	M*	45312.4	$4s^5P_2-4p^5P_3^\circ$
2205.88	10	M*	45319.2	$4s^5F_4-4p^3G_4^\circ$
2205.53	20	M*	45326.4	$4s^5P_1-4p^5P_1^\circ$
2205.09	20	M*	45335.4	$4s^5P_2-4p^5P_2^\circ$
2203.44	5	M*	45369.4	$a^3F_3-4pz^5D_4^\circ$
2202.96	100	M*	45379.3	$a^3F_4-4p^5F_4^\circ$
2200.42	25	M*	45431.5	$4s^5F_2-4p^3F_3^\circ$
2198.30	20	M*	45475.3	$4s^5F_3-4p^3G_3^\circ$
2193.61	100	M*	45572.7	$4s^5P_2-4p^5P_3^\circ$
2192.51	50	M*	45595.5	$4s^5P_3-4p^5P_2^\circ$
2190.69	75	M*	45633.5	$4s^5P_2-4p^5P_1^\circ$
2189.00	25	M*	45668.7	$4s^5F_4-4p^3F_4^\circ$
2187.05	25	M*	45709.4	$4s^5F_1-4p^3F_2^\circ$
2181.73	10	F	45820.8	$4s^5F_3-4p^3F_3^\circ$
2180.61	20	M*	45844.2	$4s^5P_3-4p^3P_2^\circ$
2174.94	2	M*	45963.9	$4s^5F_2-4p^3F_2^\circ$
2174.54	50	F	45972.3	$a^3F_4-4p^5F_5^\circ$
2173.33	60	M*	45997.9	$4s^5F_5-4p^3G_4^\circ$
2172.90	7	M*	46007.0	$4s^5F_4-4p^3G_3^\circ$
2158.16	2	M*	46321.2	$a^3F_4-4pz^5D_4^\circ$
2156.95	40	M*	46347.1	$4s^5F_5-4p^3F_4^\circ$
2156.69	10	M*	46352.7	$4s^5F_4-4p^3F_3^\circ$ $4s^5F_3-4p^3F_2^\circ$
2147.38	2	M*	46553.6	$a^3F_2-4p^5G_2^\circ$
2146.99	10	M*	46562.1	$4s^5F_2-4p^3D_2^\circ$
2136.50	4	M*	46790.7	$a^3F_2-4p^5G_2^\circ$
2133.47	10	M*	46857.2	$a^3F_3-4p^5G_4^\circ$
2129.17	1	M*	46951.8	$4s^5F_3-4p^3D_3^\circ$
2125.87	3	M*	47024.6	$4s^5F_1-4p^3D_2^\circ$
2117.95	8	M*	47200.4	$a^3F_3-4p^5G_3^\circ$
2114.40	2	M*	47279.7	$4s^5F_2-4p^3D_2^\circ$
2111.46	50	M*	47345.5	$a^3F_4-4p^5G_5^\circ$
2105.49	2	M*	47479.8	$4s^5F_1-4p^3D_1^\circ$
2105.34	3	M*	47483.1	$4s^5F_4-4p^3D_3^\circ$
2097.12	5	M*	47669.3	$4s^5F_3-4p^3D_2^\circ$
2094.24	1	M*	47734.8	$4s^5F_2-4p^3D_1^\circ$
2091.09	6	M*	47806.7	$a^3F_4-4p^5G_4^\circ$
2065.55	50	M*	48397.7	$a^3F_3-4p^3G_4^\circ$
2063.80	35	M*	48438.8	$a^3F_2-4p^3G_3^\circ$
2058.84	30	M*	48555.5	$a^3F_4-4p^3G_5^\circ$
2050.75	10	F	48746.8	$a^3F_3-4p^3F_4^\circ$
2049.19	2	M*	48784.1	$a^3F_2-4p^3F_3^\circ$

TABLE IV. *Continued.*

λ(Air)	Int.	Auth.	ν(Vac.)	Combination
2036.61	3	M*	49085.4	$a^3F_3-4p^3G_3^\circ$
2027.08	20	M*	49316.1	$a^3F_2-4p^3F_2^\circ$
2025.80	10	M*	49347.2	$a^3F_4-4p^3G_4^\circ$
2022.35	20	M*	49431.4	$a^3F_3-4p^3F_3^\circ$
2011.52	5	F	49697.8	$a^3F_4-4p^3F_4^\circ$
2000.80	10	F	49963.7	$a^3F_3-4p^3F_2^\circ$
1997.93	3	F	50035.5	$a^3F_4-4p^3G_3^\circ$
1984.21	1	F	50381.5	$a^3F_4-4p^3F_3^\circ$
1974.38	1	F	50632.2	$a^3F_2-4p^3D_2^\circ$
1956.78	30	F	51087.6	$a^3F_2-4p^3D_1^\circ$
1949.46	20	F	51279.5	$a^3F_3-4p^3D_2^\circ$
1940.64	50	F	51512.3	$a^3F_4-4p^3D_3^\circ$

M—Meggers
M*—Meggers corrected
F—Author

equation to correct the calculation such that it may more nearly conform to results obtained from a Ritz formula, these ionization potentials become, respectively, 16.7 and 17.1 volts, which are in practically exact agreement with H. N. Russell's[6] predictions.

Table IV gives all the identified lines of the spectrum.

In conclusion, I wish to thank Professor A. G. Shenstone for valuable aid and suggestions and Dr. W. F. Meggers for the use of his measurements and intensity estimates.

[6] H. N. Russell, Astrophys. J. **66**, 1 (1927).

THE SPECTRA OF GASES LIGHTED WITH STRONG ELECTRICAL DISCHARGES*

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Abstract

Spectra of condensed discharges through hydrogen at pressures up to several cm of mercury showed, as usual, the Balmer lines merging into the continuous spectrum. With increasing strength of the discharge the Balmer lines widened, the higher members of the series disappeared and the continuous spectrum became more intense, until with 1 microfarad at 15 kilovolts there were no Balmer lines left at all, only the continuous spectrum and some absorption lines due to aluminum from the electrodes, etc. Helium, oxygen and nitrogen exhibited similar changes, i.e., with increasing intensity of the discharge in helium the lines gave way to a continuous spectrum, and in oxygen and nitrogen the molecular bands gave way to spark lines and these in turn to a continuous spectrum. The continuous spectra from all the gases were alike. The intensity distribution across the continuous spectrum was rather even and hardly that of a black body. In the strong discharges the external characteristics of the atoms were pretty well effaced and the conditions perhaps approached those in the interior of a star.

IT IS known that the spectrum of a gas varies with the pressure of the gas and with the type of electrical excitation, for example, the Balmer lines of hydrogen broaden with increasing pressure and intensity of the discharge. The experiments described in this paper were undertaken to find out what the spectrum of the gas is like when very strong discharges are used.

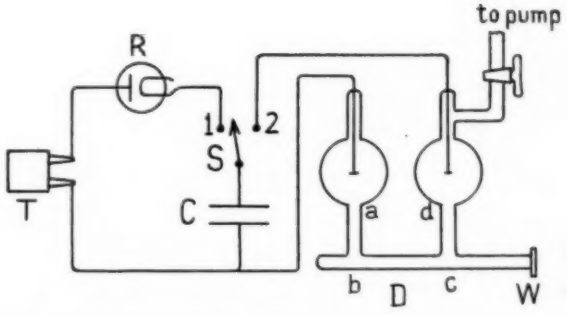

Fig. 1. Apparatus for sending strong discharges through the tube *D*.

A discharge tube *D*, Fig. 1, was arranged to be excited either directly by a 15000 volt, 25 cycle transformer *T*, or by a 0.002 microfarad condenser in series with a quenched gap to insure abrupt discharges, or by a 1 microfarad condenser. Fig. 1 gives a diagram of the apparatus for the last case.

* Published with the permission of the Navy Department.

of hydrogen widened with increasing pressure, as in strip *a* Fig. 2, the members of the series below H_7 disappeared and the continuous spectrum increased in intensity. With the 1 microfarad condenser and a discharge tube of 8 mm internal diameter between *b* and *c*, Fig. 1, there were only four Balmer lines left, these being much widened, and the continuous spectrum was intense, as in strip *b*. With the 1 microfarad condenser and a discharge tube of 4 mm internal diameter between *b* and *c*, Fig. 1, there were no Balmer lines left at all, only the continuous spectrum, as in strip *c*. The continuous spectrum was crossed by a few absorption and emission lines. Most of these were aluminum lines, but not all of them were identified. The spectra with the 1 microfarad condenser discharges were much the same for gas pressures from 20 to 60 mm of mercury, as might be expected on the idea that under such violent excitation the momentary pressure in the path of the discharge was very high and not dependent to a great extent on the pressure of the cold gas. Pressures greater than about 80 mm of mercury could not be used, for at greater pressures the discharge would not pass through the tube with the potentials available. It is interesting to compare strip *c* with strip *d* which is the spectrum of an uncondensed discharge through hydrogen at a pressure of 58 mm of mercury. This appears, except for its weakness at wave-lengths greater than 5000A, much like strip *c*. The conditions of excitation of the gas for the two spectra were as different as could well be imagined, the one being a brilliant flash and the other a gentle blue glow, and yet the continuous spectra are somewhat similar.

Helium, nitrogen and oxygen, strips *e* to *k*, Fig. 2, exhibited changes similar to those of hydrogen, i.e. with increasing intensity of the discharge in helium the lines gave way to a continuous spectrum, and in oxygen and nitrogen the molecular bands gave way to spark lines and these in turn to a continuous spectrum. The continuous spectra from all the gases with the 1 microfarad condenser discharge were closely alike. A comparison with the lines of a mercury spectrum whose intensities were known[2] showed that the distribution of intensity across the continuous spectra was constant within two, and probably one, orders of magnitude from λ6000 to 2000A. Thus, within the fairly large error of measurement, the intensity distribution did not seem to be that of a black body.

The general result of the experiments appeared to be that under the strong discharges the external characteristics, such as energy levels, etc., of the atoms of the gases were pretty well effaced. The atoms could no longer radiate their usual line or band spectrum but only a continuous spectrum. We may imagine that the conditions approached those in the interior of a star. It seems difficult at the present time to form a satisfactory quantitative theory of the continuous spectrum. In trampling on the atom we have at the same time trampled on theories of atomic behavior. It is hoped to extend the investigation using greater dispersion.

[2] Hulburt, Phys. Rev. **32**, 593 (1928).

COMPUTATION OF THE EFFECTIVE CROSS SECTION FOR THE RECOMBINATION OF ELECTRONS WITH HYDROGEN IONS

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Abstract

The quantum-mechanical computation or the cross-section for combination of electrons with a positive point charge has been carried out in polar coordinates. This gives the fraction of the recombination to a final state of total quantum number n arising from recombination to the substates of different l values, making possible a comparison of the results with the experimental recombination intensities for alkali vapors to which the theory applies approximately.

AN ELECTRON passing by a hydrogen ion with a velocity equivalent to V volts can undergo a spontaneous transition to one of the states of a hydrogen atom. The probability with which such a process can occur has been treated by Kramers[1] and by Eddington[2] by the methods of the old quantum theory and the correspondence principle. Oppenheimer[3] gives in his treatment of the motion of electrons in a Coulomb field the corresponding wave-mechanical expressions. The following paper gives certain additional calculations and numerical expressions for the probability of capture of electrons.

We recall the definition of the effective cross section of recombination: The decrease of the number N_+ ions per cm³ is expressed by

$$\frac{dN_+}{dt} = -\alpha(v)\cdot N_+\cdot N_- = -q(v)\cdot N_+\cdot N_-' \tag{1}$$

N_- is the number of electrons per cm³ having a velocity v relative to the ions. $N_-'=v\cdot N_-$ is the intensity of a stream of N_-' electrons per cm² per sec. $\alpha(v)$ is called the coefficient of recombination and $q(v)$ the effective cross section of recombination.

To find the probability of a transition of such an electron to one of the discrete states with negative energy one computes first the matrix element of the electric moment associated with the transition under consideration. As wave function in the initial state we require a solution $\psi_k(r, \cos\theta, \phi)$ of the wave equation in the force field of an ion of charge $Z\cdot\epsilon$, which becomes a plane wave at infinite distance, representing a stream along the x axis of N_-' electrons per cm² per sec.:

$$\lim_{r\to\infty}\psi_k = C\cdot\left\{e^{i(Z/ka_0)x} + \frac{f(\cos\theta)}{r}\cdot e^{i(Z/ka_0)r}\right\} \tag{2}$$

[1] Kramers, Phil. Mag. **46**, 836 (1923).
[2] Eddington, Internal Constitution of Stars, Cambridge (1926).
[3] Oppenheimer, Zeits. f. Physik **55**, 725 (1929).

and

$$\lim C \cdot \frac{h}{2\pi mc} \cdot \text{imag}\,(\bar{\psi}_k \operatorname{grad} \psi_k) = N_-'$$

$$k^2 = \frac{R_v Z^2}{V} \tag{3}$$

V is the energy of the electrons and R_V is the ionization energy of a hydrogen atom in volts. a_0 is the radius of the first Bohr orbit in hydrogen. In the final state we take the known solution of the wave equation in polar coordinates $\psi_{n,l,m}(r, \cos\theta, \phi)$. Then we compute the matrix elements in the complex rectangular coordinates

$$\left.\begin{aligned} x &= r\cos\theta; & X^2(k, nlm) \\ u &= r\sin\theta \cdot e^{i\phi}; & U^2(k, nlm) \\ v &= r\sin\theta \cdot e^{-i\phi}; & V^2(k, nlm) \end{aligned}\right\} = \int \begin{matrix} x \\ u \\ v \end{matrix} \bar{\psi}_k \psi_{nlm} d\tau_x \int \begin{matrix} x \\ \bar{u} \\ \bar{v} \end{matrix} \psi_k \bar{\psi}_{nlm} d\tau \tag{4}$$

$$d\tau = \rho^2 \sin\theta d\rho d\theta d\phi$$

The relation between the matrix element $X(k, nlm)$ and the number of transitions per sec $q_x(k, nlm)\, N_-'$ giving light of frequency ν_n polarized in the x direction is

$$q_x(k, nlm) \cdot N_-' = \frac{64\pi^4}{3} \cdot \left(\frac{\nu_n}{c}\right)^3 \frac{\{\epsilon \cdot X(k,\ nlm)\}^2}{h} \cdot \tag{5}$$

Similar expressions hold for u and v. The total cross section for any given state n, l is

$$\begin{aligned} q(k, nl) &= q_x(k, nl0) + q_u(k, nl-1) + q_v(k, nl+1) \\ &= q_x + 2q_u. \end{aligned}$$

Oppenheimer[4] computed by this method the $q(k, 10)$ and showed that it is asymptotically, for small velocities of the electron, proportional to Z^2/V. In a later paper he treated the problem for the excited states in parabolical coordinates[5] using a wave function by Gordon[5] and Temple,[6] which satisfies Eq. (2). This method gives the expression of the total cross section summed over all l's with the same n. The writers made use of the wave function used by Mott[7] for the scattering of α-particles by nuclei in order to obtain the individual $q(nl)$'s. Mott's formula is in this notation:

$$\psi_k = i \cdot \left(\frac{N_-' \cdot h}{2\pi Z\epsilon^2}\right)^{1/2} \cdot \frac{k^{1/2} \cdot e^{(k\pi/2) + ik\log\rho}}{\sinh \pi k} \cdot \tag{6}$$

$$\sum_{\lambda=0}^{\lambda=\infty} \frac{i^\lambda \cdot (\lambda + 1) \cdot P_\lambda(\cos\theta)}{\Gamma(\lambda + 1 + ik)} \cdot \rho^\lambda \cdot \oint e^{\rho z} \cdot \left(z - \frac{i}{2}\right)^{\lambda - ik} \cdot \left(z + \frac{i}{2}\right)^{\lambda + ik} \cdot dz$$

[4] Oppenheimer, Phys. Rev. **31**, 349 (1928).
[5] Gordon, Zeits. f. Physik **48**, 180 (1928).
[6] Temple, Proc. Roy. Soc. **121A**, 673 (1928).
[7] Mott, Proc. Roy. Soc. **118A**, 542 (1928).

$\rho = (2Z/ka_0)\cdot r$ and the integral is to be taken along a single contour around $z = \pm i/2$. The asymptotic expansion for $r = \infty$ satisfies Eq. (2), having however in the first exponent an additional slowly varying logarithmic term (see Oppenheimer[4] and Mott[7]). The evaluation of the integrals in Eq. (4) is done following a method given by Fues[8] and used for similar problems by Oppenheimer.[9] At one step one is left with an integral

$$J(k) = \oint \frac{\left(z - \frac{i}{2}\right)^{\lambda - ik}\left(z + \frac{i}{2}\right)^{\lambda + ik}}{\left(-z + \frac{k}{2n}\right)^{l+\lambda+s+4}}\, dz$$

to be taken around $z = k/2n$. Its evaluation leads to the formulas 7*a* and 7*b*. for $q_x(nl)$ and $q_u(nl)$. 7*c* and 7*d* are the formulas taken from Oppenheimer's paper.[3]

Abbreviating: R for the Rydberg constant in frequency units

$$Q(\lambda, \alpha) = \sum_{p=0}^{p=\alpha} \binom{\lambda - ik}{p}\binom{\lambda + ik}{\alpha - p}\left(\frac{n + ik}{-n + ik}\right)^{(\alpha/2)-p},$$

$$S(k, l) = \frac{k^{2l+6}}{k^2(k^2 - 1^2)(k^2 - 2^2)\cdots(k^2 - (l-1)^2)},$$

$$T(k) = \frac{e^{\pi k - 4k\tan^{-1}(n/k)}}{\sinh \pi k},$$

$$D = \frac{32\cdot\pi^5}{3}\cdot\frac{a_0^5 R^2}{Z^2 c^2}$$

$$F(\alpha\ \beta\ \gamma\ ) = 1 + \frac{\alpha\cdot\beta}{1\cdot\gamma}\cdot z + \frac{\alpha(\alpha+1)\cdot\beta(\beta+1)}{1\cdot 2\cdot\gamma(\gamma+1)} z^2 + \cdots$$

$$q_x(n,l) = D\cdot\frac{\nu_n}{c}\cdot\frac{(n-l-1)!}{(2l+1)\cdot(n+l)!\,n^{2l+4}}\cdot S(k,l)\cdot T(k)$$

$$\cdot\left\{\sum_{s=0}^{s=n-l-1}\left(\frac{2}{n}\right)^s\left(\frac{R\cdot Z^2}{\nu_n}\right)^{s/2}\cdot\frac{(2l+2+s)!}{s!}\binom{n+l}{n-l-1-s}\right. \tag{7a}$$

$$\cdot\left[\frac{4l}{k^2}\,\frac{RZ^2}{\nu_n}\cdot Q(l-1, 2l+2+s) - \frac{(2l+s+3)(2l+s+4)(l+1)}{(l+ik)(l+1+ik)}\right.$$

$$\left.\left.\cdot Q(l+1, 2l+4+s)\right]\right\}^2$$

[8] Fues, Ann. d. Physik **81**, 422 (1926).
[9] Oppenheimer, Zeits. f. Phvsik **41**, 268 (1927).

$$q_u(n,l) = q_v(n,l) = D\cdot\frac{\nu_n}{c}\cdot\frac{(l+1)!(n-l-1)!}{(l-1)!(2l+1)\cdot(n+l)!n^{2l+4}}S(k,l)\cdot T(k)\cdot$$

$$\left\{\sum_{s=0}^{s=n-l-1}\left(\frac{2}{n}\right)^s\left(\frac{R\cdot Z^2}{\nu_n}\right)^{s/2}\cdot\frac{(2l+2+s)!}{s!}\binom{n+l}{n-l-1-s}\right. \tag{7b}$$

$$\left.\left[\frac{4}{k^2}\cdot\frac{RZ^2}{\nu_n}O(l-1,2l+2+s)+\frac{(2l+s+3)(2l+s+4)}{(l+ik)(l+1+ik)}\cdot Q(l+1,2l+4+s)\right.\right.$$

$$q_z(n) = \sum_{l=0}^{l=n-1}q_z(n,l) = 64D\cdot\frac{\nu_n}{c}\cdot\frac{k^6}{(n^2+k^2)^2}\cdot T(k)$$

$$\sum_{s=0}^{s=n-1}\left|(n-s-1)\cdot F\left(-ik,2+s-n,1,\frac{-4ink}{(n+ik)^2}\right)\right. \tag{7c}$$

$$\left.-\left(n-s-1-\frac{2ink}{n+ik}\right)F\left(-ik,1+s-n,1,\frac{-4ink}{(n+ik)^2}\right)\right|^2$$

$$q_u(n) = q_v(n) = \sum_{n=0}^{n=l-1}q_u(nl) = 64D\cdot\frac{\nu_n}{c}\cdot\frac{(4n)^2k^{10}}{(n^2+k^2)^4}\cdot T(k).$$

$$\sum_{s=0}^{s=n-2}(s+1)(n-s-1)\left|F\left(1-ik,2+s-n,2,\frac{-4ink}{(n+ik)^2}\right)\right|^2. \tag{7d}$$

For electrons whose kinetic energy is small compared with the term value of the final state, we substitute $w=z/k$ in the integral $J(k)$ and obtain

$$J(k) = k^{\lambda-l-s-3}\oint\frac{w^{2\lambda}\cdot e^{-1/w}\cdot dw}{\left(-w+\frac{1}{2n}\right)^{l+\lambda+s+4}}.$$

This integral is to be taken around the point $w=1/2n$ and is independent of k. Instead of formulas 7*a* and 7*b* be obtain 8*a* and 8*b*. 8*c* and 8*d* are the corresponding asymptotic expressions for $k=\infty$ of Eq. (7c) and (7d). For all states we obtain $q=A\cdot 10^{-20}\cdot Z^2/V$ for small V. Since in experiments on recombination the electron velocities are usually small, these formulas are sufficient in most cases.

Abbreviating

$$K(l,\lambda) = \sum_{\alpha=0}^{\alpha=l}\binom{l}{\alpha}\binom{2\lambda}{\alpha}\frac{\alpha!}{(2n)^\alpha}\cdot\sum_{\beta=0}^{\beta=l-\alpha-1}\binom{l-\alpha}{\beta}\binom{l-\alpha-1}{\beta}\frac{\beta!}{(-2n)^\beta}$$

$$E = \frac{4^7\cdot\pi^5}{3c^3}\cdot a_0^5R^3R_v = 1.24\times 10^{-19}\,\mathrm{cm^2\,volt}$$

$$M(l,\lambda) = \sum_{\alpha=0}^{\alpha=l}\binom{l}{\alpha}\frac{(-4n)^\alpha}{(\alpha+\lambda)!}$$

we obtain

$$q_x(nl) \sim \frac{E\cdot Z^2}{V}\cdot\frac{(n-l-1)!16^l\cdot n^{2l+2}}{(2l+1)\cdot(n+l)!e^{4n}} \tag{8a}$$
$$\left\{\sum_{s=0}^{s=n-l-1}\frac{(4n)^s}{s!}\binom{n+l}{n-l-s-1}\left[l\cdot R(2l+s+2,l-1)+(l+1)\cdot R(2l+s+4,l+1)\right]\right\}^2$$

$$q_u(nl) = q_v(nl) \sim \frac{EZ^2}{V}\cdot\frac{l(l+1)\cdot(n-l-1)!16^l\cdot n^{2l+}}{(2l+1)\cdot(n+l)!e^{4n}}$$
$$\cdot\left\{\sum_{s=0}^{s=n-l-1}\frac{(4n)^s}{s!}\binom{n+l}{n-l-s-1}\left[K(2l+s+2,l-1)\right.\right. \tag{8b}$$
$$\left.\left.-K(2l+s+4,l+1)\right]\right\}^2$$

$$q_x(n) = \sum_{l=0}^{l=n-1} q_x(n,l) \sim \frac{EZ^2}{V}\cdot\frac{1}{4n^2\cdot e^{4n}}\cdot$$
$$\cdot\sum_{s=0}^{s=n-1}\left\{(n-s-1)\cdot M(n-s-2,0)+(n+s+1)\cdot M(n-s-1,0)\right\}^2 \tag{8c}$$

$$q_u(n) = q_v(n) = \sum_{l=0}^{l=n-1} q_u(n,l) \sim \frac{E\cdot Z^2}{V}\cdot\frac{4}{e^{4n}}$$
$$\cdot\sum_{s=0}^{s=n-2}(s+1)\cdot(n-s-1)\cdot M(n-s-2,1)^2. \tag{8d}$$

Empirical formulas are generally written in a form

$$q(n,l) = \text{const}\times\frac{1}{V\cdot\nu_{nl}{}^s}, \tag{9}$$

where ν_{nl} is the frequency of the emitted light, given for hydrogen by

$$\nu_{nl} = \nu_n = RZ^2\left(\frac{1}{n^2}+\frac{1}{k^2}\right). \tag{10}$$

$s=2$ for the $2P$ band of Cs I (see report on recombination by Mohler[10]). Evaluating Eq. (8) for some of the lower states and abbreviating the algebraic expressions of k in frequencies according to Eq. (10) one obtains formulas 11, where

$$B = \frac{2\cdot 4^5\cdot\pi^5}{3}\cdot\frac{a_0\cdot R^5\cdot R_v\cdot Z^6}{c^3}.$$

[10] Mohler, Phys. Rev. Supplement 1, 216 (1929).

$$
\begin{cases}
1s:\ q = q_x(10) = B\cdot T(k)\cdot \dfrac{1}{V\cdot \nu_1^2} \\
2s:\ q = q_x(20) = \dfrac{B\cdot T(k)}{8}\cdot \dfrac{\nu_1}{V\cdot \nu_2^3} \\
3s:\ q = q_x(30) = \dfrac{B\cdot T(k)}{27}\cdot \dfrac{\nu_1\cdot \nu_i^2}{V\cdot \nu_3^5};\ i = \left(\dfrac{27}{7}\right)^{1/2} \sim 2 \\
2p:\ q = q_x(21) + 2q_u(21) = B\cdot T(k)\cdot \dfrac{RZ^2\left(\dfrac{1}{36}\dfrac{\nu_j}{\nu_2} + \dfrac{1}{8}\right)}{\nu_2^3};\ j = \tfrac{2}{3}
\end{cases}
\tag{11}
$$

This shows that the empirical way of writing the formulas involves frequency terms without physical meaning. The general form of the expressions (11) however is similar to Eq. (9), as T varies only slowly with k. None of these functions shows any maximum point corresponding to the results of Davis and Barnes experiment,[11] nor do any of the curves for higher states.

From formulas 8*a* and 8*b* the constants $A(nl)$ were computed for some of the lower states. The complexity of the sums increases greatly with larger n's. Fig. 1 compares the exact and the asymptotic expressions for the 1*s*

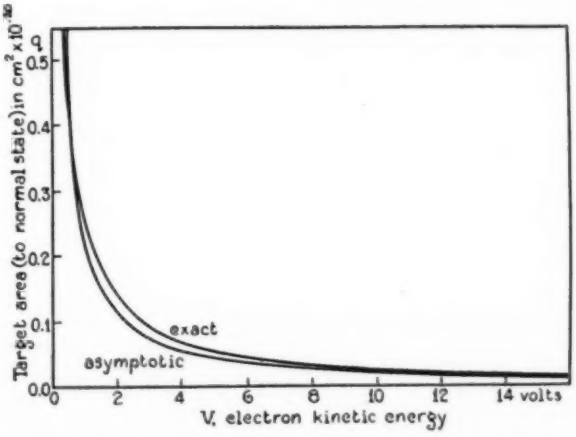

Fig. 1. Exact and asymptotic values of q for recombination to the 1*s* state.

state. Table I and Fig. 2 give the values of $A(n)$ for 1*s*, 2*s*, 2*p*, 3*s*, · · · , to 5*s*. The values of $\Sigma_l A(nl)$ is given in the last column of Table I and plotted as black dots in Fig. 2. The $\Sigma_l A(nl)$ have been computed by summing over the $A(nl)$ from Eq. (8a) and (8b), and to check it, also directly by Eq. (8c) and (8d). (Oppenheimer's formulas.)

[11] Davis and Barnes, Phys. Rev. **34**, 152 (1929); Barnes, Phys. Rev. **34**, 1224 (1929); **35**, 718 (1930).

TABLE I. *Values for* $A(nl)$ *and* $A(n)=\sum_{l=0}^{l=n-1}A(nl)$ *in formula* $q(nl)=A(nl)\cdot 10^{-20}\cdot Z^2/V$ cm².

terms	s	p	d	f	
n	$A(n0)$	$A(n1)$	$A(n2)$	$A(n3)$	$A(n)$
1	.227				.227
2	.0335	.109			.143
3	.0114	.0403	.0520		.104
4	.0053	.0190	.0318	.0254	.0814
5	.0030				

For a comparison of the absolute magnitude of the q's with the experimental values obtained from recombination spectra, we compare in Table II the values as given by Mohler[10] for the $1S$, $2P$ and $3D$ states of caesium for $V=0.2$ volts with the states $2s$, $2p$, $3d$ of hydrogen. There is little justification for picking these hydrogen states as comparison, except that their

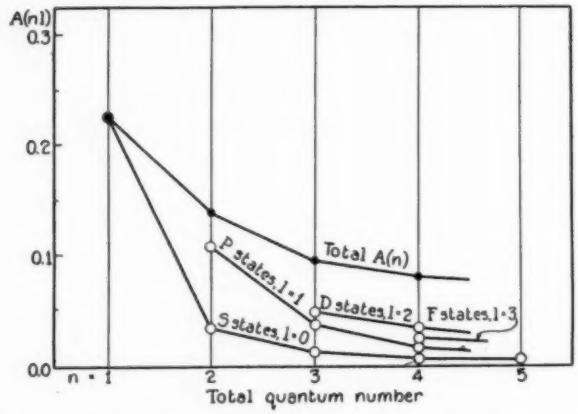

Fig. 2. Values of A in the formula $q=A\times 10^{-20}\ Z^2/V$ for recombination to various states.

effective quantum numbers most nearly correspond. For the P and D state we have a satisfactory agreement. The discrepancy of the $1S$ value is to be expected, since it is a highly penetrating orbit, and therefore would differ from a hydrogen-like behavior in a much greater degree than the P and D states. A similar disagreement is pointed out by Mohler[10] in comparing the continuous absorption of these states with the theoretical computations for

TABLE II. *Comparison of values of q for V=0.2 volts between caesium (experimental data) and hydrogen (theoretical data).*

	Cs		H
term	q	term	q
$1S$	0.015×10^{-21} cm²	$2s$	1.7×10^{-21} cm²
$2P$	6.0×10^{-21} cm²	$2p$	5.5×10^{-21} cm²
$3D$	6.0×10^{-21} cm²	$3d$	2.6×10^{-21} cm²

the same hydrogen states by Oppenheimer.[9] If one takes the states $6s$, $6p$ and $5d$ of hydrogen, whose *true* quantum numbers are the same as for the series electron of Cs in the considered states, the correspondence is improved with respect to the S-state (it being wrong by a factor 10 instead of 100) but the agreement for the P- and D-states is worse by a factor of about 10. This comparison is not given in Table II, because these higher terms have not been computed but only roughly extrapolated

It can not be expected to have any better agreement than this, since the wave function of the series electron in Cs is considerably different from that of any state in hydrogen. It is interesting to see that the best agreement for the P and D states is obtained by comparison with hydrogen states of the same effective quantum number.

Attempts to find an expression for the total target area

$$q = \frac{\sum_{n,l} A(nl) \times 10^{-20} \times Z^2}{V}$$

have not been successful.

The experiments by Davis and Barnes[11] can not be explained through spontaneous recombination of the electrons and α-particles and must therefore be due to some other mechanism.

THE RECOMBINATION OF IONS IN ARGON, NITROGEN AND HYDROGEN

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Abstract

Since free electrons are known to exist in ionized A, N_2 and H_2 these gases are employed in an effort to measure directly the coefficient of recombination for positive ions and electrons. At the same time the coefficient is determined for positive and negative ions in H_2 which would be expected theoretically to differ from other gases. The method is one using x-rays as the ionizing agent and has already been described by L. C. Marshall and the writer. Previous indirect methods and theory indicate that α, the coefficient of recombination for ions and electrons is of the order of 10^{-10} compared to 10^{-6} for positive and negative ions. In the present work results similar to those in air are obtained in the pure gases, and only a slight change in α is observed when sufficient O_2 is added to cause immediate attachment of the free electrons. Further direct tests in pure A, N_2 and H_2 indicate that negative ions are present in large quantities at all times, although a constant number of free electrons is also present. Hence it is probable that recombination was taking place between positive and negative ions rather than positive ions and electrons. It is assumed that as a result of the action of the ionizing agent negative ions are formed by attachment to excited metastable molecules in the case of A and N_2 and by attachment to atoms or triatomic molecules in the case of H_2.

In accordance with the criterion established in a previous paper for air, "absolute values" of α are set as follows:

Gas	*Coefficient of Recombination*
Air	$1.4 \pm 0.1 \times 10^{-6}$
O_2	$1.5 \pm 0.1 \times 10^{-6}$
A	$1.2 \pm 0.1 \times 10^{-6}$
N_2	$1.2 \pm 0.1 \times 10^{-6}$
H_2	$0.32 \pm 0.05 \times 10^{-6}$

The results in H_2 show a constant value of $0.32 \pm 0.05 \times 10^{-6}$ which is much lower than in the other gases contrary to the prediction of the J. J. Thomson theory of recombination. However, the theory is deficient in certain respects which may explain this discrepancy.

Introduction

THE present work on the recombination of ions produced by x-rays is a continuation of previous investigations by L. C. Marshall[1] and the writer.[2] This second part was undertaken in an effort to measure directly the coefficient of recombination of positive ions and electrons, and at the same time to determine the coefficient of recombination in H_2 which would be expected to differ from other gases. Gases were used in which free electrons

[1] L. C. Marshall, Phys. Rev. **34**, 618 (1929).
[2] O. Luhr, Phys. Rev. **35**, 1394 (1930).

are known to exist for considerable periods of time. Thus in A, N_2 and H_2 free electrons will not attach to the normal molecules, but may attach to excited molecules or to molecules of impurity which may be present.

Theoretically it is to be expected that recombination between electrons and positive ions would proceed very slowly compared to that between negative and positive ions.[3] This has in general been born out by numerous indirect spectroscopic methods of measurement[4] and in one case by the direct measurements of Atkinson[5] whose results, however, were inconclusive. Kenty,[6] using spectroscopic methods and the Langmuir probe estimated the coefficient in very pure A to be of the order of 10^{-10} compared to 10^{-6} for positive and negative ions. Marshall,[1] with practically the same apparatus as that used by the writer believed he had found evidence of a low coefficient of recombination in pure A since the value was only about half that obtained when one cm partial pressure of O_2 had been added to the pure gas. The one cm of O_2 was sufficient to cause immediate attachment of all the free electrons present. Marshall used a metal ionization chamber where it is impossible to obtain the best conditions of purity, and he believed that the recombination in pure A was taking place principally between positive ions and negative ions formed by attachment of electrons to molecules of impurity.

In the present work it was found that Marshall's results were partially in error due to an unshielded lead (from the commutator to the ionization chamber) which caused a small statically induced charge to remain on the lower plate of the ionization chamber. No such effect was to be expected since the lead and lower plate were grounded through a half megohm resistance. However, because of the very high potentials in the room from the x-ray equipment, there was actually sufficient field to draw out most of the free electrons in 0.15 seconds, though there was no appreciable effect on the ions. Marshall attributed this loss of electrons to diffusion, but very little loss was observed in the present work even after a second, when the lead was shielded by enclosing it in a grounded metal tube. Also, the coefficient of recombination remained approximately the same when sufficient partial pressure of O_2 was added to any of the gases to obtain immediate attachment of the free electrons. This might indicate that the coefficient of recombination for positive ions and free electrons is nearly the same as for positive and negative ions, but it is believed that actually a considerable number of free electrons were attaching, possibly to impurities, but more likely to metastable excited molecules produced by the ionizing agent.

Method of Measurement and Preliminary Experiments

The apparatus has already been described by Marshall[1] and the writer,[2] and was used in exactly the same form in the present work. It consists of a rotating shutter and commutator mechanism which furnishes a means of

[3] L. B. Loeb, Trans. Am. Electrochem. Soc. **LV**, 131 (1929).
[4] R. Seeliger, Phys. Zeits. **30**, 329 (1929).
[5] R. d'E. Atkinson, Zeits. f. Physik **51**, 188 (1928).
[6] C. Kenty, Phys. Rev. **32**, 624 (1929).

ionizing the gas in the ionization chamber by a flash of x-rays, then measuring the charge remaining at any time afterward by a suitable adjustment of the commutator and brushes. A sufficiently high field is applied to the lower plate of the ionization chamber through the commutator to produce a saturation current, thus sweeping all the ions of one sign to the upper plate almost instantly at any desired time. A neutralizing current is forced through a high resistance carbon line leak by means of a potentiometer, thus keeping the upper plate and electrometer system always at zero potential during the flash time and time of recombination.

The method of calculation is also the same as before, all values of α, the coefficient of recombination—obtained from the equation $\alpha = 1/t(1/n - 1/n_0)$—being determined as a function of τ the age of the ions rather than t the total time of recombination.[2] In some cases this produced rather irregular results due to the very small differences in the potentiometer readings when the time of recombination was of the order of a few thousandths or a hundredth of a second. Thus very small errors in taking the potentiometer readings, due principally to fluctuations in intensity of the x-rays caused large errors in the values of α, and the plotted points do not always lie as close to a smooth curve as would be desired. However, since this method of calculation gives the only true picture of what is happening at any particular time, it was thought best to use it throughout.

Two small though important changes were made in the method of measurement. Instead of making use of the total volume of the ionization chamber ($10 \times 20 \times 7.5$ cm), the defining slit at the front of the chamber was narrowed down so that a beam of x-rays about 2.5 cm instead of 7.5 cm high passed between the plates. The volume of ionization was thus kept about 2.5 cm from each plate so that the possibility of diffusion of electrons to the plates with a resulting spuriously high coefficient of recombination would be at a minimum. On a kinetic theory basis it may be estimated that an electron would, on the average, diffuse a distance of two or three cm in as little as one-tenth of a second. However, this is extremely unlikely in the present case since the space charge produced by the positive ions remaining in the volume of ionization would prevent the electrons from diffusing to any great extent. Nevertheless, it was actually found in tests on A that the coefficient of recombination dropped off about fifteen percent as the distance of the x-ray beam from the plates was increased to a maximum.

The other change in the method of measurement consisted in having the sector opening the same for every run regardless of the commutator speed. This was necessary to produce sufficient ionization for convenient measurement. The sector opening was only 18° for A due to the intense ionization and 90° for air, N_2 and H_2. Thus effectively older ions and more random distribution occurred at faster commutator speeds. Hence, α dropped more rapidly with time though the initial and final values remained the same as before, as shown by a comparison of the results in air obtained with the two methods. The situation was further aggravated by the high intensities of x-radiation which were necessary to produce sufficient ionization in H_2 and

N_2. As a result it is more difficult to set an "absolute value" for the coefficient of recombination as was done for air,[2] since the point at the end of the sharp drop due to nonrandom distribution is not clearly defined.

As in the previous work on air and O_2, all values of α are corrected for diffusion by assuming a swelling of the volume of ionization given by,

$$V = V_0 + 2A(\overline{\Delta x})_\tau$$

where V_0 is the initial volume, A is the area of the upper plate of the ionization chamber and $(\overline{\Delta x})_\tau$ is the average distance an ion will diffuse in time τ given by $(\overline{\Delta x})_\tau = (4D\tau/\pi)^{1/2}$ from the Brownian movement equation.[7] D is the coefficient of diffusion given by $D = 0.0236k$ where k is the mobility of the ions. For air, A and N_2 the average mobility is about 2 cm per second per volt per cm, or D is 0.047. The mobility in H_2 is of the order of 6 cm per second giving D as 0.142. Owing to the use of a relatively small volume of ionization (though it was still 448 cm^3 or seven times as large as that used by Marshall) the diffusion corrections were of the order of twenty percent at the longest time intervals but this correction gave results apparently consistent with the previous ones in air using larger volumes.

One extraneous effect observed in pure A, N_2 and H_2 is worthy of note. While Marshal was continually losing free electrons until there were very few left after 0.15 seconds, in the present work the negative readings were in general about three percent higher than the positive. This effect was evidently due to the presence of free electrons since the positive and negative readings became equal if sufficient O_2 was added to produce attachment. It was apparently not caused by a residual field as in Marshall's case since it was purely a percentage effect not varying with time. This possibility was further investigated by allowing x-rays to pass into the chamber with no field present to sweep out the ions. No appreciable charge was built up on the upper plate as long as the shielded lead was employed, but if the unshielded one used by Marshall was inserted a large positive charge accumulated indicating the loss of electrons to the lower plate. It was thought that possibly scattered radiation from the x-ray beam was in some way producing an excess of negative charges by photoelectric action on the metal surfaces, but photographs of the beam emerging from the ionization chamber showed it to be very sharply defined with no indication of any scattered radiation. The explanation may lie either in the presence of contact potentials or in a slight distortion of the field producing weak curved lines of force outside the volume of ionization which would sweep electrons of high mobility but not negative ions to the upper plate. The effect was not considered to be serious, however, since the positive readings were always used in calculating the coefficient of recombination. The negative readings would in general have given slightly higher values of α indicating a very small loss of electrons by diffusion from between the plates.

In regard to the purity of the gases, extreme care was taken so that the possibility of attachment of free electrons to molecules of impurity was

[7] L. B. Loeb and L. C. Marshall, Jour. Frank. Inst. **207**, 371 (1929).

reduced to a minimum. The ionization chamber was thoroughly cleaned with cleaning solution to remove any organic materials. The A, N_2 and H_2 were first passed over copper heated to 400°C to remove the oxygen. They were then subjected to the same treatment as the air by passage through glass wool, sodium calcium hydrate, $CaCl_2$, P_2O_5 and two liquid air traps. The A, which was the purest obtainable in large quantities contained considerable N_2 as indicated by the presence of N_2 bands in the spectrum. Otherwise the gases were spectroscopically pure showing no evidence of organic compounds or oxygen when the discharge was observed with a large direct vision spectroscope.

Direct tests for the presence of free electrons. In view of the unexpectedly high values of α obtained in pure A, N_2 and H_2 it was thought desirable to test further for the presence of free electrons. In order to accomplish this a second brush was added to the commutator system so that an alternating potential could be applied to the lower plate of the ionization chamber. Thus by keeping the volume of ionization close to the lower plate and varying the driving and retarding potentials, the apparatus could be used to measure mobilities by the simple Rutherford alternating current method.[8] Although the measurements were somewhat complicated by the presence of positive ions, the results in every case indicated two facts:(1) Only a part of the negative carriers were free electrons (probably twenty to forty percent) when the age of the ions was about 0.01 seconds, the newest that could be studied; (2) The total number of electrons remained approximately the same as the ions aged to 0.5 seconds or more, although a considerable portion of the negative carriers had disappeared by recombination. Thus negative ions and free electrons were probably both present in large quantities during the period of recombination, but there was no gradual attachment of free electrons taking place as would be expected if impurities were present. This can only lead to the conclusion that most of the attachment occurred within a few thousandths of a second after the formation of the ions, which would result if the effect were due to metastable excited molecules produced by the ionizing agent. This question will be considered further in the discussion of the results.

Experimental Results

Values of the coefficient of recombination obtained in pure argon are shown in Fig. 1. The different curves correspond to commutator speeds varying from 16 to 1/2 revolutions per second. The initial concentration of the ions varied from about 2.5×10^6 ions per cm^3 at 16 revolutions per second to 1.1×10^7 ions per cm^3 at 1/2 revolution per second. The initial value of α at a time of 0.002 seconds is about 1.6×10^{-6}, and the value then drops off in a manner similar to that in air to about 0.55×10^{-6} at 0.75 seconds. A similar series of runs was next taken with the addition of 2 cm partial pressure of O_2 added to the A. This was sufficient to cause almost instant attachment of the

[8] J. J. Thomson, Conduction of Electricity Through Gases, p. 102, III Edition, Cambridge 1928.

free electrons as indicated by the equality of the positive and negative readings. The results, however, (which are not shown in the diagrams)

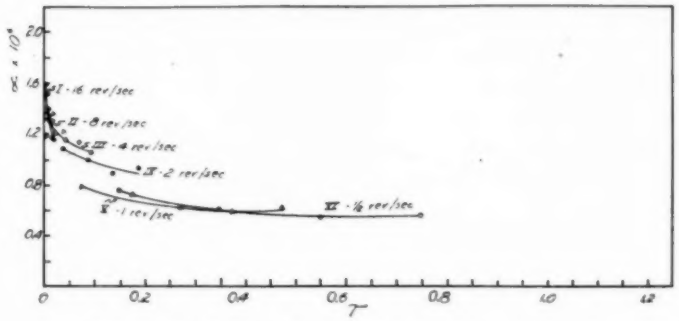

Fig. 1. Coefficient of recombination for pure argon.

were exactly the same as for pure A within the limits of experimental error except at the very shortest time interval (0.002 seconds) where $\alpha = 1.7 \times 10^{-6}$

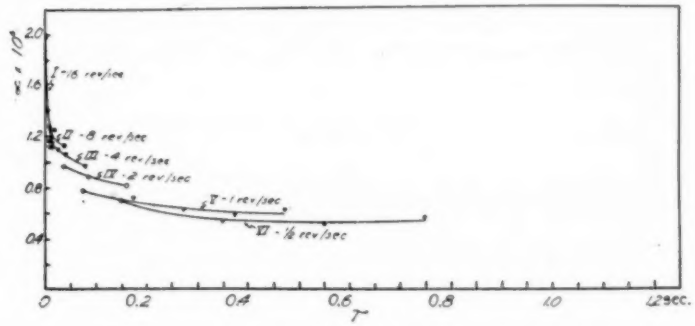

Fig. 2. Coefficient of recombination for argon with 15 cm partial pressure of O_2.

instead of 1.6×10^{-6}. With the possibility that insufficient O_2 had been added, another series of runs was taken with 15 cm partial pressure of O_2 correspond-

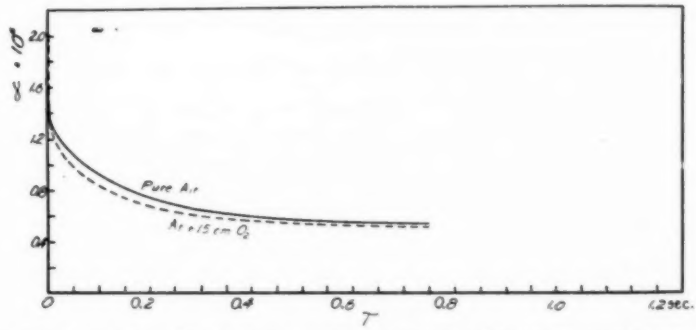

Fig. 3. Comparison of results in pure argon and argon with 15 cm partial pressure of O_2.

ing to the $N_2 - O_2$ mixture in air. The results shown in Fig. 2 were again almost the same as in pure A except at the very shortest time when $\alpha = 2.0$

$\times 10^{-6}$. A comparison of the results obtained with pure A and A+15 cm O_2 are shown in Fig. 3. Average values of α for any particular age τ are plotted against τ. The A+O_2 curve starts higher, crosses the pure A curve at about 0.005 seconds and continues on slightly lower for the remainder of the time.

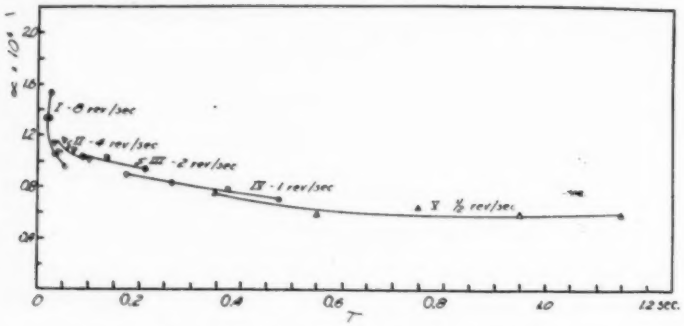

Fig. 4. Coefficient of recombination for pure nitrogen.

Fig. 4 shows the results for pure N_2 which are not far different from the corresponding values for A. It was impossible to obtain accurate results at the fastest commutator speed (16 revolutions per second) owing to the lack of sufficient concentration of ions. Even at 8 revolutions per second (time of

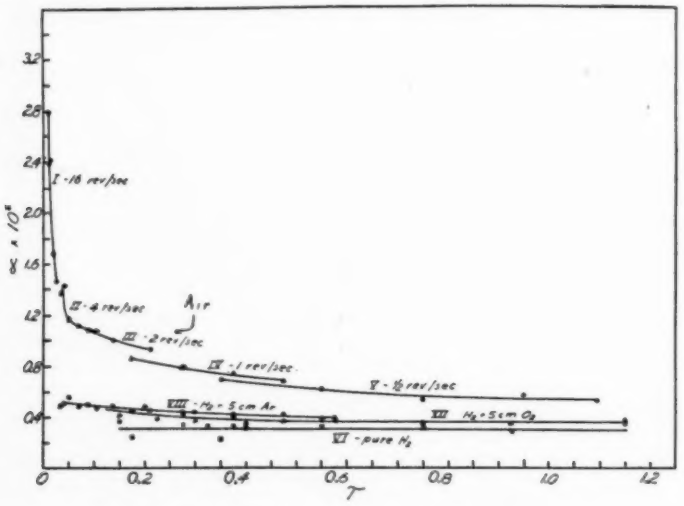

Fig. 5. Results for air and hydrogen.

exposure to x-rays 0.0156 seconds) the concentration was only 0.91×10^6 ions per cm³ which gave rather inaccurate values of α.

Fig. 5 gives the results for air and H_2. Curves I to V were taken in air for varying commutator speeds under the conditions corresponding to those for A and N_2; i.e. with constant sector opening of 90° and as high initial concentration as possible. The initial concentration varied from 0.79×10^6 ions per cm³ at 16 revolutions per second to 4.8×10^6 at 1/2 revolution per

second. The value of α varies from 2.8×10^{-6} at $\tau=0.008$ seconds to 0.55×10^{-6} at $\tau=1.15$ seconds.

Curve VI, Fig. 5 gives the results for pure H_2, showing a constant value of 0.32×10^{-6} for α between 0.15 and 1.15 seconds. Owing to the extreme difficulty of obtaining sufficient concentration of ions, no runs at commutator speeds faster than one revolution per second could be taken. Even at one revolution per second (time of exposure to x-rays 0.25 seconds) only 0.46×10^{6} ions per cm³ were obtained. At 1/2 revolution per second the initial concentration was 0.90×10^{6} ions per cm³. Argon in varying quantities was then added to the H_2 to obtain greater concentration of ions, but made no appreciable difference in the value of α up to 5 cm partial pressure. The results for 5 cm partial pressure of A with H_2 are shown in Curve VIII, Fig. 5. The values of α are only slightly higher than for pure H_2, starting at about 0.50×10^{-6} at $\tau=0.03$ seconds (commutator speed 4 revolutions per

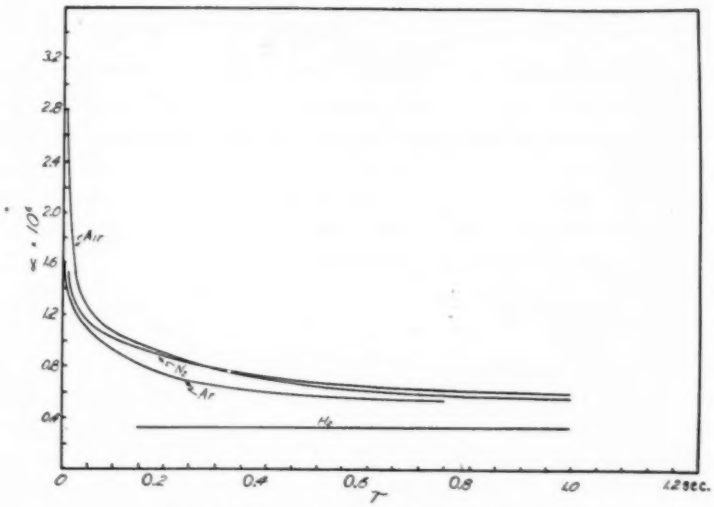

Fig. 6. Comparison of results for pure gases.

second) and dropping to 0.40×10^{-6} at $\tau=0.6$ seconds. Runs at commutator speeds of 1 and 1/2 revolutions per second were next taken with 5 cm partial pressure of O_2 added to pure H_2 to obtain attachment of the free electrons. The results (Curve VII, Fig. 5) again show only a small change from those in pure H_2, α dropping from 0.45×10^{-6} at 0.15 seconds to 0.35×10^{-6} at 1.15 seconds. A final series of runs was taken with 5 cm partial pressure of A and 5 cm of O_2 added to pure H_2 but gave results identical with those for 5 cm partial pressure of A (Curve VIII).

A comparison of the results for air, pure A, pure N_2 and pure H_2 are given in Fig. 6. As in Fig. 3 average values of α are plotted against τ the age of the ions. Except at the shorter time intervals the results show a marked similarity for air, N_2 and A despite the fact that free electrons in large quantities were undoubtedly present in the N_2 and A. The values of α for H_2 are strikingly lower than those for the other three gases.

Discussion of Results

From the results in the preceding section four facts stand out clearly:

(1) The coefficient of recombination for pure A and N_2 where free electrons should be present is only slightly lower than for air except at very short time intervals (probably 0.05 seconds or less) when random distribution of the ions has not been attained.

(2) The coefficient of recombination in pure H_2 is much lower than in the other three gases having approximately a constant value of 0.32×10^{-6}.

(3) The addition of sufficient O_2 to cause instant attachment of free electrons in A, N_2 and H_2 increases the value of α at the very shortest time intervals.

(4) In A and N_2 the addition of O_2 apparently results in a slight lowering of the values of α after random distribution has been attained.

Regardless of the question of recombination between positive ions and free electrons, one definite conclusion may be drawn from these facts. When free electrons are present, the value of α is lower at the very short time intervals indicating that random distribution is attained more rapidly. This is of course to be expected since electrons would diffuse evenly throughout the volume much more quickly than negative ions and the so-called initial recombination would not occur to as great an extent.

Interpretation of results in A and N_2. In regard to the question of recombination between positive ions and electrons the results are inconclusive. If theory and previous spectroscopic results are to be relied on, α should be so small (of the order of 10^{-10}) that no recombination could be observed in the present work where the concentration of ions is of the order of 10^6 per cm^3. Either, then, the spectroscopic results (obtained at low pressures and generally in the presence of rather high fields) are not applicable here, or else recombination was occurring in the present case only between positive and negative ions. If α for positive ions and electrons is very low, and attachment were taking place gradually, the curves would be expected to start at a low value of α for short times, then increase as time goes on until all the free electrons had attached. However, no such low value of α at short time intervals was observed, the values actually increasing rapidly down to 0.002 seconds. Finally, then, one of two conclusions may be drawn: either recombination between positive ions and free electrons is as rapid as that between positive and negative ions, or else a large portion of the free electrons had attached in less than 0.001 seconds. The second view is strongly supported by the evidence obtained in the tests for the presence of free electrons which have already been described.

In view of the precautions taken to obtain pure gases, and the results of the tests for free electrons which indicated that a definite number of electrons were present at all times, it does not seem likely that many electrons had attached to molecules of impurity in 10^{-3} seconds. Nevertheless, such a conclusion might conceivably be in error. As already mentioned there is however another mechanism by means of which attachment might have

taken place in A and N_2. The intense hard x-rays and fast β-particles produced by them undoubtedly excite a large number of molecules. If these excited molecules remain in metastable states for a considerable period of time (as in the case of active N_2) impacts between the excited molecules and free electrons could give a means of dissipating the electron energy and allow attachment to form negative ions. An effect of this kind has been observed by da Silva[9] who found some attachment in N_2 and H_2 which had been ionized by α particles. A similar process might occur in A which also has metastable states. On the other hand Loeb[10] and Cravath[11] observed no attachment in these gases where the electrons had been produced by ultraviolet light and hot filaments.

Interpretation of results in H_2. Hydrogen presents a different problem from A and N_2 since metastable excited states do not exist. However, attachment may still take place to atoms or triatomic molecules as indicated by the results of da Silva. Observations in H_2 by Langevin,[12] Townsend[13] and McClung[14] indicated that the coefficient of recombination was slightly lower than in air (1.4×10^{-6} compared to 1.6×10^{-6}) while in the present work α was found to be 0.32×10^{-6} for H_2 cmpared to 1.4×10^{-6} for air. The present results may be assumed more reliable owing to the improvements in technique now possible. On the other hand, J. J. Thomson's theory of recombination as modified by Loeb and Marshall[7] gives much higher values of α for H_2 than for air, even assuming the molecular weight of the ions to be 32(since the negative ion is ordinarily a molecule of impurity such as O_2). In this case it turns out that α is 2.34×10^{-6} compared to 1.62×10^{-6} for air. If the molecular weight is taken as 2.016, α is 9.50×10^{-6}. Since in pure H_2, α is observed experimentally to be much lower than in air, this might be taken as an indication of the presence of a preponderance of free electrons which would recombine slowly. However, the addition of sufficient O_2 to produce attachment of the electrons should then bring the value of α up at least as high as for air, probably higher. As shown in Fig. 5 very little change was observed. The theory, however, is based on the assumption that if both ions suffer a single impact when they are within a defined distance d of each other they will lose all the excess kinetic energy gained as a result of their mutual attractions since the last impact. This single impact is assumed a sufficent condition for recombination. Since the mass of the ions is probably large compared to that of the molecules, a single impact may not suffice to remove the excess energy and the ions my drift apart without recombining. In other words, several impacts are probably required to reduce the excess energy, which fact cannot be taken into consideration by the theory as it stands. In this way α could be less for H_2 than for air in agreement with the experimental results.

[9] M. A. da Silva, Ann. de Physique **12,** 100 (1929).
[10] L. B. Loeb, Kinetic Theory of Gases, p. 507, New York, 1927.
[11] A. M. Cravath, Phys. Rev. **33,** 605 (1929).
[12] P. Langevin, Ann. de Chim. et de Phys. **28,** 433 (1903).
[13] J. S. Townsend, Phil. Trans. Roy. Soc. **A193,** 157 (1900).
[14] R. McClung, Phil. Mag. **3,** 383 (1902).

Thus, in view of the experimental facts it is probable that the recombination observed in this work was taking place between positive and negative ions rather than positive ions and free electrons The negative ions may have been formed by attachment of electrons to impurities but the evidence points strongly to the supposition that the attachment was to metastable excited molecules in the case of A and N_2, and to atoms or triatomic molecules in the case of H_2.

Values of the recombination coefficient in various gases. As indicated earlier it is more difficult to set an "absolute value" of α in this work than in the previous work on air owing to unfavorable experimental conditions. However, if the value of α for air is taken as $1.4 \pm 0.1 \times 10^{-6}$ at the point where the sharp drop due to non-random distribution ends, and the more gradual drop due to aging begins, comparison of the curves in Fig. 6 indicates a value of $1.2 \pm 0.1 \times 10^{-6}$ for A and N_2. The value for H_2 may be more definitely set as $0.32 \pm 0.05 \times 10^{-6}$ since in this case there is no appreciable change with time.

A list of values for the coefficient of recombination determined by the above criterion for all the gases studied may then be given as follows:

Gas	*Coefficient of Recombination*
Air	$1.4 \pm 0.1 \times 10^{-6}$
O_2	$1.5 \pm 0.1 \times 10^{-6}$
N_2	$1.2 \pm 0.1 \times 10^{-6}$
A	$1.2 \pm 0.1 \times 10^{-6}$
H_2	$0.32 \pm 0.05 \times 10^{-6}$

In conclusion the writer wishes to express his sincere thanks to Mr. N. E. Bradbury for assisting in taking the readings and to Professor Loeb for his inspiring guidance throughout the course of these experiments.

THE MOBILITIES OF IONS IN DRY AND MOIST AIR

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Abstract

With the method recently described the distribution of mobilities of aged ions in dry air has been determined and the values for moist air remeasured because of a neglected correction in the previous results. In air dried by passage through metal tubes and filters immersed in liquid air the negative ions were found to consist of two main groups of which the less numerous group comprises about one third of the total number of ions and has a peak mobility only about 60 percent of that of the main group. The number of ions in the lesser group was relatively smaller in air dried by calcium chloride alone and their presence in still smaller numbers in air having a water content of 2 mg per liter accounts for the dissymmetry in the distribution curves of negative ions in moist air reported in the previous paper. The distribution curves for positive ions in dry air also show some indications of two groups of ions only here the ions of the less numerous group, which does not appear in moist air, have a peak mobility about 40 percent higher than those of the main group. The absolute values of the peak mobilities found for the main group of negative ions in the driest air used for a pressure of 76 cm and a temperature of 20°C was 2.45 cm/sec. This diminished to 2.37 cm/sec for air dried by calcium chloride, and to 2.08 cm/sec for air containing 2 mg of water per liter. Under the same conditions the mobilities of the positive ions increased in succession from 1.05 cm/sec to 1.10 cm/sec to 1.36 cm/sec. These large opposite changes produced by a small fraction of one percent of water molecules can only be explained on the supposition that aged ions in air consist of molecular clusters whose structure is affected by the presence of water molecules. The second group of negative ions cannot consist of ions having multiple electronic charges, because the mobility of these ions is smaller than that of the main ion group. It cannot arise from the presence of impurities condensable at liquid air temperatures. Since electrons do not readily become attached to nitrogen molecules, the central molecule of each of these ions is probably an oxygen molecule and the two cluster groups may arise either from a difference caused by a different point of attachment of the electron to the central molecule or from the nature of the molecule that first becomes attached to this central molecule in the process of cluster formation.

IN a recent paper[1] I reported some results on the mobilities of well-aged ions in moist air which showed that the ions of each sign are not all alike. No distinct groups were resolved but the mobilities in each case were found to be spread continuously over a range of values. Within this range, the positive ions as regards numbers present were distributed quite symmetrically about a most numerous kind, while the negative ions had mobility values extending much farther in the direction of lower mobilities than in the direction of higher mobilities.

[1] J. Zeleny, Phys. Rev. **34**, 310 (1929).

The method employed in the mobility measurements has some distinct advantages over other methods which have been used, and the work with it has now been extended to dry air.

The new results disclose for negative ions in very dry air a second group of ions comprising about one-third of the total number and having a mobility only about six-tenths of that of the ions in the main group. Indications of this new group in smaller numbers are well marked in air dried by passage through calcium chloride alone, and the presence of these ions in still smaller numbers also accounts for the lack of symmetry mentioned above in the distribution curves for negative ions in moist air.

Some indication too was found that among positive ions in very dry air a second group of higher mobility than that of the main group is also present.

The peak mobility of the main group of positive ions was found to decrease quite markedly when the air was dried, while that of the main group of negative ions increases with removal of moisture.

The method used consists in blowing a nonturbulent stream of air between two concentric cylinders, admitting ionized air into this stream through small openings in the outer cylinder, and measuring the distance the ions are carried down stream while they are crossing the space between the two cylinders under the action of an applied field.

The average velocity of the main air stream with which the velocity of the ions was compared was maintained throughout these measurements at approximately 8 cm/sec. This low velocity is well within the limits of nonturbulent motion in the apparatus used. The potentials used on the outer cylinder were such as allowed the ions in crossing to be carried down stream only far enough to permit an accurate determination of the distance, in order to keep the correction for ion diffusion as small as possible.

Reference should be made to the previous paper[1] for details regarding the apparatus and for the procedure used in reducing the observations, as well as for references to the work of other observers.

A few modifications were made in the apparatus. The connecting tubes were all made of metal or glass. The openings in the outer cylinder through which the ionized air is admitted into the main gas stream were enlarged and now consist of 20 slots along a circumference, each slot being 1 mm wide and 9 mm long. The total area of these openings is now such that with a stream of ionized air delivering 9.8 cc per sec. as was used throughout these measurements the correction which has to be applied to mobility determinations to allow for the penetration of this ion stream into the main air current is on the average less than one-half of one percent.

The movement of the inner cylinder with its insulated ion collector ring is now effected by a threaded micrometer head working on a rod extending from the system to be moved to the outside of the apparatus. This improvement makes possible more rapid and more accurate settings of the ion collector ring.

The radioactive material used for producing ions in the auxiliary chamber during these measurements consisted of a deposit of polonium on a nickel

strip which was wound around the outside of the outer cylinder a short distance up stream from the openings through which the ions entered the main gas stream. The polonium coating was sealed gas tight by a covering of thin condenser paper.

The age of the ions as they entered the main gas stream was on the average about 3 sec. although some of the ions were only about 1 sec. old.

The air for the main gas stream was supplied by the pressure system of the laboratory. To dry the air, it was passed in succession through a large filter, through a 16 cm wide bottle containing granulated calcium chloride, through a second filter, through a long copper coil of small diameter immersed in liquid air, and finally through a second copper coil immersed in a water bath maintained at room temperature. The air for the auxiliary ion bearing stream was passed through a similar, separate drying system. In some of the last measurements, additional filters immersed in liquid air were added to the drying system. These contained first a section filled with coarse metal filings to ensure a closer contact between the cold surfaces and the air, and then closely packed glass wool to remove any crystals of ice which might be blown along by the stream and later be changed to vapor.[2]

Measurements of the mobilities of both positive and negative ions were made not only in air dried as has just been described, but also in air dried much less thoroughly by calcium chloride alone, and in undried air of low but determined humidity. These last measurements are included because the absolute values given in my last paper for the mobilities in moist air are somewhat low owing to the fact that the air pressure at the gauge used for measuring the stream velocity was unwittingly allowed to exceed the limit within which no correction for this pressure had to be made. A mercury manometer, previously removed to avoid the presence of mercury vapor, was now kept at this gauge and the gauge was recalibrated for the same gas pressures as were used in the measurements.

Air Dried by Aid of Liquid Air

Curve *A* of Fig. 1 gives an example of the way in which negative ions were found distributed along the inner cylinder, when the air used was dried as described above by passage through calcium chloride and through a long helical tube immersed in liquid air. The abscissas give the down stream distances from the place of entry of the ions into the air stream and the ordinates give the corresponding ion numbers. The difference of potential between the two cylinders was 12 volts. The curve of distribution is a compound one, and by drawing the two branches *c* and *d*, the sum of whose ordinates for any abscissa is equal to the corresponding ordinate of the experimental curve, the compound curve may be resolved into two simple curves having peaks at *a* and *b*. The observed distribution thus shows the presence of two distinct groups of ions, of which those of higher mobility are about twice as numerous as those of lower mobility. Some of the other

[2] H. A. Erikson, Phys. Rev. **34**, 642 (1929).

similar observations show a small number of ions carried even farther down stream than is here apparent, indicating ions of still lower mobility. The mobility corresponding to the peak of the less numerous group of ions was found to be on the average 1.45 cm/sec. which is about six-tenths of the value for the main group.

Curve *B* of Fig. 1 is an example of corresponding results obtained for positive ions. The difference of potential between the cylinders was 15 volts. The main air stream and the ion bearing stream as well were passed in this case through calcium chloride and tubes immersed in liquid air and subsequently through a cylindrical metal box, also immersed in liquid air, which contained a layer of fine metal turnings and closely packed glass wool.

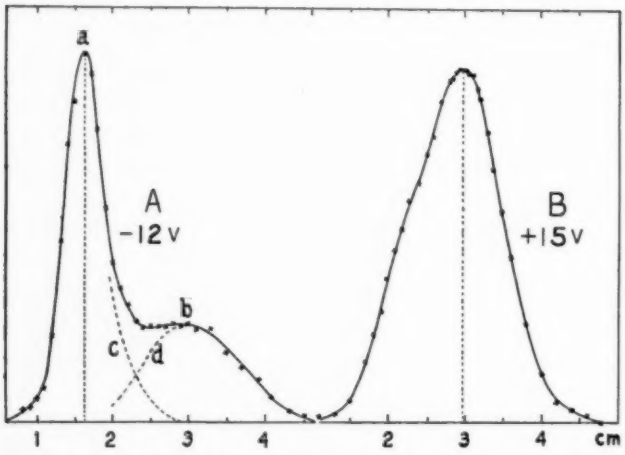

Fig. 1. Distribution of ions in dry air. Ordinates represent number of ions corresponding to down stream distances given as abscissas. Curve *A* is for negative ions in air dried by passage through tubes immersed in liquid air. Curve *B* is for positive ions where a filter immersed in liquid air was added to the drying system.

Curve *B* shows an entirely different distribution of ions than that found for negative ions. The dotted ordinate drawn through the peak of the curve shows that now the number of ions on the upstream side of the peak is greater than on the downstream side. There is a bulge in the curve near the abscissa distance 2.2 cm which appears also in all of the other similar observations, indicating the possible presence of an unresolved group of ions having a peak mobility of about 1.5 cm/sec., the mobility of the ions at the main distribution peak being here only 1.06 cm/sec.

A summary of the mobilities found for the peak of the distribution curves of the main group of ions in air dried by use of liquid air is given in Table I. The uncorrected potential of the outer cylinder relative to the inner one is indicated in each case. These results, as well as all others to be given, have been reduced to a temperature of 20°C and a pressure of 76 cm of mercury.

The unusually large difference between the positive and negative mobilities is to be noted. This difference is much larger than can be accounted for according to prevailing theories by a difference of mass alone. Linear dimen-

TABLE I. *Peak mobilities of predominant group of ions in very dry air.*

(a) Air dried by $CaCl_2$ and tubes in liquid air.			
+12 volts	1.10 cm/sec.	−12 volts	2.40 cm/sec.
+15 "	1.06 "	−15 "	2.38 "
+20 "	1.07 "	−10 "	2.41 "
Positive ions	1.08 cm/sec.	Negative ions	2.40 cm/sec.
(b) Air dried by $CaCl_2$ and tubes and filters in liquid air.			
+15 volts	1.04 cm/sec.	−15 volts	2.45 cm/sec.
+15 "	1.05 "	−15 "	2.44 "
+15 "	1.06 "		
+15 "	1.04 "	Negative ions	2.45 cm/sec.
Positive ions	1.05 cm/sec.		

sions of the ions must be invoked as a prominent factor in determining such variation in mobility.

The presence of the extra filters immersed in liquid air appears to have resulted in a more complete drying of the air, since the positive ion mobilities in (b) the lower portion of the table are on the average a little smaller than in (a) the upper portion, and those of the negative ions are a little larger. The amount of water remaining in the air after the above treatment must be very small. The computed amount at −194°C given in the International Critical Tables is 1.6×10^{-23} mg per liter; naturally such a low value cannot be approximated in the apparatus used.

The total spread of ions when they arrive at the inner cylinder as shown by the curves of Fig. 1 does not represent altogether ions of different mobilities. A part of the spread arises from diffusion and mutual repulsion of the ions during their passage between the two cylinders. A method of correcting for these effects is fully described in my previous paper,[1] and when applied to the results for positive ions shows that ions are present ranging in mobility from 0.83 cm/sec. to 1.58 cm/sec., the two possible groups present being treated as one. Owing to the partial overlapping of the two groups of negative ions, the spread of mobilities in the main group having the faster ions can only be obtained for the upstream side of the peak. The fastest ions here were found to have a mobility 11 percent greater than the peak mobility. In the group of lower mobility the estimated spread on either side of the peak mobility is between two and three times the above value.

The high value of the peak mobility of negative ions here given is in agreement with that obtained by Schilling[3] likewise in very dry air but for ions of lesser age. The mobility of the positive ions here found for very dry air is lower than values hitherto reported. It must be remembered that this value corresponds to the peak of a distribution curve which shows strong indications of a less numerous group of higher mobility. Schilling makes note of the fact that the curves he obtained with positive ions, using the alter-

[3] H. Schilling, Ann. d. Physik **83**, 23 (1927).

nating field method, were of a form to be expected from a mixture of different ions.

Air Dried by Granulated Calcium Chloride

A number of measurements were made with air dried by passage through granulated anhydrous calcium chloride only, this being known as a rather poor drying agent and leaving in air water to an amount of about 0.2 mg per liter.[4]

Examples of the ion distribution curves obtained under these conditions are given in Fig. 2, where curve *A* represents negative ions and curve *B* positive ions, the voltage used being 15 volts in each case.

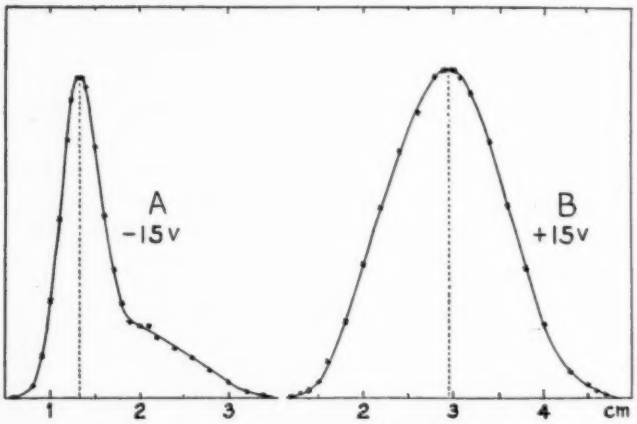

Fig. 2. Distribution of ions in air dried by calcium chloride. Curve *A* = negative ions. Curve *B* = positive ions.

The curve for the negative ions, in addition to the main group represented by the high peak, also shows the existence of ions of a smaller mobility but these are less numerous than was found to be the case (curve *A*, Fig. 1) with air more completely freed of water molecules.

The curve for the positive ions does not show the bulge seen on curve *B* of Fig. 1, although the dotted ordinate drawn through the middle of the peak helps to show the presence here also of a larger number of ions of mobility greater than the most numerous kind than there are of ions with a smaller mobility.

Table II. *Peak mobilities of ions in air dried by calcium chloride alone.*

+15 volts	1.10 cm/sec.	−12 volts	2.38 cm/sec.
+12 "	1.12 "	−20 "	2.33 "
+15 "	1.08 "	−10 "	2.35 "
+15 "	1.09 "	−15 "	2.41 "
+15 "	1.09 "		
+15 "	1.13 "	Negative ions	2.37 cm/sec.
Positive ions	1.10 cm/sec.		

[4] A. T. McPherson, Jour. Am. Chem. Soc. **39**, 1317 (1917).

Table II gives a summary of the results for the peak mobilities of ions in air of this degree of dryness.

The values for the positive ions are here a little larger and those for the negative ions somewhat smaller than those given in Table I.

The positive ion group was found to extend between the same limits as given above for positive ions in air dried by aid of liquid air. The main negative ion group extends from a peak mobility of 2.37 cm/sec. up to 2.54 cm/sec. The presence of a group or groups of negative ions of lower mobility here also prevents the getting of an estimate of the value of the lower limit of the mobilities in this main group.

Air with Average Water Content of 2 mg/liter

Fig. 3 gives examples of the distributions found for ions in filtered air drawn directly from the pressure system of the laboratory, and containing on the average 2 mg of water per liter. The air for the auxiliary stream in

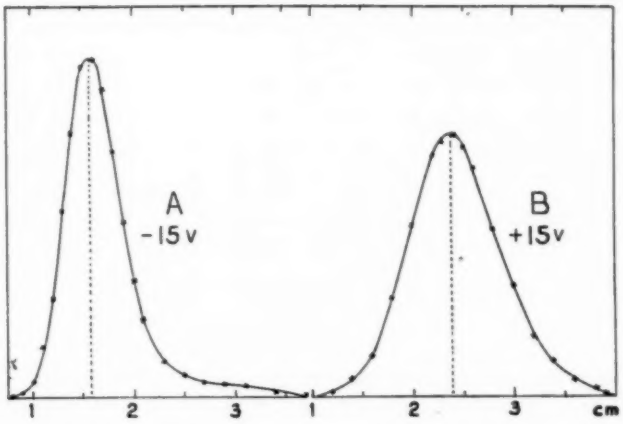

Fig. 3. Distribution of ions in air having a water content of 2 mg per liter. Curve *A* = negative ions. Curve *B* = positive ions.

which the ions were produced was supplied by a gasometer containing water and carried on the average 13.6 mg of water per liter. As this air did not mix with the main air stream, it is probable that the mobilities obtained are the same as would have been obtained had the ion bearing stream contained the same amount of water as was present in the main stream.

The positive ion distribution curve *B* shows the ions to be almost equally distributed on the two sides of the peak value. The negative ion curve *A* is again far from symmetrical but the group of ions of lower mobility, clearly indicated in Figs. 1 and 2, here shows only as an extended foot of the curve for the main ion group. It appears therefore that this low mobility group of ions forms a smaller and smaller portion of the whole number as the amount of water present in the air is increased. Its presence accounts for the lack of symmetry, reported in the previous paper, in the distribution curves for negative ions in moist air. The positive ions are spread over a somewhat smaller range of values here than is the case in dry air.

A summary of the results for moist air is given in Table III.

TABLE III. *Peak mobilities in moist air.*

Potential	Water content	Mobility	Potential	Water content	Mobility
+15 volts	1.90 mg/l	1.36 cm/sec.	−12 volts	1.45 mg/l	2.08 cm/sec.
+ 8 "	1.90 "	1.40 "	−15 "	1.98 "	2.05 "
+20 "	1.90 "	1.35 "	−12 "	1.98 "	2.07 "
+15 "	1.98 "	1.34 "	−12 "	1.74 "	2.12 "
+12 "	1.98 "	1.35 "			
+15 "	1.33 "	1.37 "		Negative ions	2.08 cm/sec.
+15 "	2.89 "	1.38 "			
	Positive ions	1.36 cm/sec.			

The water content of the air used in the main gas stream is given in milligrams per liter in the second and fifth columns. The water molecules in the stream formed only about one quarter of one percent of the total number and yet their effect on the mobilities of the ions is seen, by comparison with the values of Table I, to be quite marked, the positive ion mobilities being increased by about 30 percent and the negative ions decreased by about 18 percent relative to those obtained in the driest air used. It is not possible to account for these large opposite effects on the two ions by an increase in the resistance to their motion due to the presence of the water molecules. It is necessary therefore to postulate that aged ions consist of molecular clusters and that the water molecules produce a change in their structure, such that the size of the positive ion cluster is diminished and that of the negative ion increased.

The increase in the mobility of positive ions produced by the presence of water molecules as given above confirms my earlier results and is in agreement with the results of Blanc[5] and Laporte[6] for ions of lesser age. Several other observers have obtained an opposite effect of moisture upon the mobility of positive ions, but it must be noted that in general the ions used have been much less aged than was the case in the experiments being reported. Valta[7] using very young positive ions found their mobilities to decrease both with age and with water content of the air and has obtained in very dry air values as high as 6.8 cm/sec. Nolan and Nevin[8] found remarkable fluctuations in the values of the mobilities of ions of both signs as the water content of the air was increased. It is difficult to reconcile all of these different experimental results on the effect of moisture on ionic mobilities in air.

The results given above clearly show the presence of two groups of aged negative ions in very dry air. The group of lower mobility has about one-half as many ions as the one of higher mobility. The relative number of these slower ions is considerably smaller in air dried by calcium chloride alone, and is still less in air having a water content of 2 mg per liter.

[5] A. Blanc, Jour. de Physique **7**, 825 (1908).
[6] M. Laporte, Ann. de Physique **8**, 466 (1927).
[7] Z. F. Valta, Journal of Geophysics and Meteorology (Russian) **6**, 197 (1929).
[8] J. J. Nolan and T. E. Nevin, Proc. Roy. Soc. **A127**, 155 (1930).

It is of theoretical interest that among aged ions it is possible under any circumstances for two distinct groups of small ions to coexist. It is improbable that the new group consists of ions with multiple charges which tend to become reduced to unit charges in the presence of water molecules, since all of the evidence points either to an increase of mobility with increase of charge or to an independence of mobility of the ionic charge. The presence of some unusual impurity might be thought to give rise to the new ion group. If such an impurity consisted of vapors coming from the compression pump or elsewhere, we should expect its effect to be least pronounced or absent when the air was passed through tubes immersed in liquid air where such vapors would be condensed, whereas the opposite was found to be the case.

It is probable therefore that the two negative ion groups under discussion consist of clusters of molecules the center of each of which is a molecule of one of the chief constituents of the atmosphere, to which an electron has become attached. Since electrons do not attach themselves readily to nitrogen molecules the central molecules are probably oxygen molecules. The evidence available is not sufficient to account satisfactorily for the two negative ion groups, but we may suppose that the difference in cluster size arises either from a difference in place of attachment of the electron to the molecule or from a difference in the kind of molecules that by chance first become joined to the central charged molecules during the formation of the clusters.

I am indebted to Mr. R. S. Baldwin and to Mr. C. D. Bock for aid with the measurements.

EXCITATION PROCESSES IN THE HOLLOW CATHODE DISCHARGE

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Abstract

The low potential gradients in the negative glow in a hollow cathode discharge in a rare gas make it a favorable source for the excitation of metallic spark spectra. The metal studied forms the cathode, and is brought into the discharge by cathode sputtering or evaporation. The excitation is limited by collisions of the second kind between gas and metal atoms and ions. The spectroscopic data of all the available cases have been examined to see what determines the processes occurring. In general only those processes occur in which the metal can be excited to some term in the spark spectrum with gain or loss of only a small amount of kinetic energy to balance the reaction equation. High melting point metals or those which sputter poorly cathodically enter the discharge in helium in the normal state or in a low metastable state of the atom. With low boiling points metals appreciable numbers of metal ions enter the reactions. In intermediate cases or in argon or neon, it is not always possible to predict if metal ions will enter the reaction or not. The conditions which determine the results are discussed.

THE excitation of metallic spectra by the discharge in a hollow cathode tube in a rare gas atmosphere has been discussed by Paschen,[1] Frerichs[2] and Takahashi.[3] While there is general agreement that the excitation is mainly limited by collisions of the second kind between rare gas atoms or ions and metallic atoms or ions there has not been agreement as to the exact nature of the collisions. Paschen and Frerichs have attributed the fundamental process to collisions between metallic ions and excited metastable rare gas atoms. Takahashi on the other hand considers only normal or metastable metallic atoms which receive energy from metastable atoms or ions of the rare gases. On the basis of somewhat more experimental material than was available at the time the discussions mentioned above were written, it is now possible as will be shown in this paper to explain the processes involved somewhat more fully and to show that under suitable conditions any of the excitations proposed by the author's mentioned may occur.

The conditions on the hollow cathode are rather different from those in other discharges. With such a cathode, often though not necessarily inside a cylindrical anode, and an applied D.C. potential of 300 or 400 volts, at a suitable pressure which depends on the cathode dimensions, the discharge is almost wholly inside the cathode. The discharge then consists of a negative dark space close to the inner wall of the cathode and a very bright negative

[1] Paschen, Sitzungsb. d. Preus. Akad. d. Wiss. p. 207 (1927).
[2] Frerichs, Ann. d. Physik 85, 362 (1928).
[3] Takahashi, Ann. d. Physik 3, 49 (1928).

glow filling the cathode. The positive column practically disappears. This discharge was first used as a spectroscopic source by Paschen.[4] It was explained by Günther-Schulze[5] who showed that when the pressure was decreased in such a tube until the mean free path of electrons leaving the inner wall of the cathode was sufficient to bring them into the positive space charge of the opposite side of the inner wall they would there reduce this charge causing an increased current and a lower cathode fall of potential inside and so setting up a condition permitting a very much greater current density from the inner wall of the cathode than from the outer. The discharge then takes place chiefly inside the cathode. The pressure at which this effect will occur depends on the diameter of the cathode and the nature of the gas. It is a pressure such that the normal cathode dark space is about equal to the inner radius of the hollow cathode. The discharge however is formed inside the cathode with an abnormal dark space thickness much less than normal. This space inside the negative glow of the hollow cathode is nearly field free and ions may exist there in considerable concentrations and radiate freely even from states of high quantum number. The negative glow in the hollow cathode is very brilliant and this light source is one of the best for exciting the first spark spectra of the metals.

The metallic atoms which enter the discharge are removed from the cathode wall by ionic bombardment and evaporation. In the analogous case of cathode sputtering Von Hippel[6] found with argon at 0.1 mm pressure in spectrograms of the light just at the cathode surfaces that the only spectral lines of the cathode material which appeared were the resonance lines of the atom. From this he concluded that the material is given off in an atomic state and arrives in the negative glow by a diffusion process. His theory is that intense local heating of the cathode by ion bombardment causes minute hot spots from which the cathode metal is evaporated. If the resonance lines of the cathode metal appear near the cathode, the cathode metal must enter the discharge as excited atoms as well as normal atoms. Ions knocked off the cathode could not normally penetrate the high cathode fall of potential in the hollow cathode (100–300 volts according to measurements of Schüler).[7] We may expect in general in the negative glow of the hollow cathode reactions with metallic atoms both neutral and excited (in metastable states) although, as will be pointed out later, under certain conditions significant numbers of metal ions may enter the reactions. These metallic particles entering the negative glow suffer collisions with rare gas particles, or with electrons whose velocity is limited by collisions with rare gas atoms. The spectrum of the negative glow shows the spectrum of the ionized exciting gas very strongly. In fact with a grating not particularly good below λ300 Sawyer and Lang[8] observed in the discharge in helium as many as four

[4] Paschen, Ann. d. Physik **50**, 901 (1916).
[5] Günther-Schulze, Zeits. f. Physik **19**, 313 (1923).
[6] v. Hippel, Ann. d. Physik **80**, 672 (1926) and **81**, 1043 (1926).
[7] Schüler, Phys. Zeits. **22**, 264 (1921).
[8] Sawyer and Lang, Phys. Rev. **34**, 712 (1928).

members of He II series 1^2S-m^2P beginning at λ304 and Paschen[9] under suitable pressure and current conditions has observed in the hollow cathode in helium Stark effect in the higher members of the helium series due to the electric fields of the great concentration of helium ions. It is then to be expected that excited atoms in the metastable state and ions in the normal state will be the predominating energy states in which the rare gas will be found and that the transfer of these energies to the metallic atoms will fix the limiting conditions of excitation for the spectrum of the metal.

To check these considerations there are available data for the hollow cathode excitation of aluminum, copper, magnesium and zinc in helium, argon and neon; cadmium in helium and argon; and gallium, mercury and thallium in helium.[10] Not all of these data are well adapted for the study of the question in hand. In some cases the investigation did not cover a sufficiently wide spectral region to permit a certain determination of the kind of excitation attained in the discharge. In others the limit attained is low and so the terms too few and too far apart to fix the limit sharply. For the sake of completeness it has, however, all been assembled.

TABLE I. *Important energy levels of metallic spectra.*[11]

Normal State of Atom				Metastable State of Atom			Normal State of Ion		
	Config.			Config.			Config.		
Al	(s^2p)	$^2P_{\frac{1}{2}}$	42280	—	—	—	(s^2)	$^1S_0$	151860
Ga	(s^2p)	$^2P_{\frac{1}{2}}$	48379	(s^2p)	$^2P_{1\frac{1}{2}}$	47552	(s^2)	$^1S_0$	165458
Tl	(s^2p)	$^2P_{\frac{1}{2}}$	49263	(s^2p)	$^2P_{1\frac{1}{2}}$	41470	(s^2)	$^1S_0$	164600
Mg	(s^2)	$^1S_0$	61663	(sp)	$^3P_0$	39813	(s)	$^2S_{\frac{1}{2}}$	121265
Cu	$(d^{10}s)$	$^2S_{\frac{1}{2}}$	62306	(d^9s^2)	$^2D_{2\frac{1}{2}}$	51105	(d^{10})	$^1S_0$	163634
Zn	$(d^{10}s)$	$^1S_0$	75759	$(d^{10}sp)$	$^3P_0$	43450	$(d^{10}s)$	$^2S_{\frac{1}{2}}$	144890
Cd	$(d^{10}s^2)$	$^1S_0$	72535	$(d^{10}sp)$	$^3P_0$	42420	$(d^{10}s)$	$^2S_{\frac{1}{2}}$	136377
Hg	$(d^{10}s^2)$	$^1S_0$	84182	$(d^{10}sp)$	$^3P_0$	46536	$(d^{10}s)$	$^2S_{\frac{1}{2}}$	151280

For each of the metals mentioned above Table I gives the electron configuration of the normal state of the ion and of the first state and of the lowest metastable state of the atom. In aluminum this metastable state is the lowest $^2P_{1\frac{1}{2}}$ of the normal configuration and is too near $^2P_{2\frac{1}{2}}$ to be differentiated in the data at hand. Table I also gives for each configuration the energy of removing the outermost electron from this configuration—that is to excite the metal to the lowest or normal state of its next ion. For con-

[9] Paschen, Sitzungsb. d. Preus. Akad. d. Wiss., p. 135 (1926).

[10] Al in He, Sawyer and Paschen, Ann. d. Physik. **84**, 1 (1927).
Hg in He, Paschen, Sitzungsb. d. Preus. Akad. d. Wiss., p. 3 (1928). and Naudé, Ann. d. Physik **3**, 1 (1929).
Cd and Zn in He, Takahashi, Ann. d. Physik **3**, 27 (1929).
Tl in He, Smith, Phys. Rev. **35**, 235 (1930).
Ga in He, Sawyer and Lang, Phys. Rev. **34**, 712 (1928).
All others, Frerichs, Ann d. Physik **85**, 362 (1928).

[11] The data in table II are taken from Paschen-Götze "Seriengesetze der Linienspektren" or from the references in footnote 10.

venience in spectroscopic discussion this value is given in ν-units. It may of course be converted to equivalent volts by multiplying by 1.2345×10^{-4}. For the three rare gases the atomic energies available are, also in ν-units

	Energy of ionization	Energy of metastable state
Helium	198308	159830 (2^3S) or 166251 (2^1S)
Neon	173930	134819
Argon	127104	94546

From the energy available from the rare gas atoms together with the data of Table II there may be calculated the highest spectroscopic state of the metal ion which should be excited by any of the probable collisions of the second kind with a rare gas. Thus for example $Zn'(d^{10}sp\,^3P_0)+He'(2^3S)\rightarrow Zn^+(?)+He(1^1S)+e$ we have:

energy to ionize metastable zinc	43450
energy to doubly ionize first zinc ion	144890
	188340
energy of He (2^3S)	159830
	28510

Thus, this reaction fails by 28510 ν-units to achieve second ionization, or a Zn II term of absolute value (measured from ionization) 28510 would just be excited. The results of such computations are listed in Table II, where in the column heads M stands for the metal concerned and G for the gas. Reactions with He′ (2^1S) are not listed. The results of a reaction with He′ (2^1S) may be obtained by subtracting 6421 from the term obtained by a reaction with He′ (2^3S).

TABLE II. *Excitation of metallic spectra in hollow cathode discharge in gases.*

	Calculated	–	Excitation	–Observed		
	M+G′	M+G⁺	M′+G′	M′+G⁺	M⁺+G′	Maximum	Limit
Al+He	40310	*1832*	—	—	−7970		1116
+Ne	65321	26210	—	—	*17041*		16943
+A	105594	73036	—	—	*57314*		56512
Ca+He	54007	*15529*	53180	*14702*	5628		12397
Tl+He	54033	*15555*	46240	7762	4770		12484
Mg+He	23098	−15380	*1248*	−37230	−38565		5419
+Ne	48109	*8928*	26259	−12922	−13534	8−10000	5419
+A	88382	55824	66532	33974	26719		17844?
Cu+He	66110	27632	54909	*16431*	3804	27−30000	16703
+A	131394	98836	120193	87635	*69088*		68837
Zn+He	60819	*22341*	28510	*−9968*	*−14940*	22−28000	−11400
+A	126103	93545	93794	61236	50344		27800?
Gd+He	49080	*10602*	18967	−19510	*−23453*	11−13000	−26800
+A	114364	81806	84251	51693	41831		46531
Hg+He	75632	*37154*	*37986*	−492	*−8550*	39−42000	−8019

The processes in italics are those which account for observed features of the spectra.

The experimental results of interest in this discussion are tabulated in the two right hand columns of Table II. In each case where it is certainly determined there is given the limit, that is, the highest spectral term of the metal ion excited in the rare gas atmosphere. There is also given any observed maximum of excitation—any terms which appear to be excited more strongly than immediately lower terms—indicating resonance phenomena in the exciting process.

A comparison of the calculated and observed excitation in Table II shows that many of the observed features of the spectra may be explained on the basis of various of the exciting processes. The cases will be discussed in order of their simplicity.

Aluminum, gallium and thallium are all high boiling point metals. Aluminum sputters cathodically less than any other metal tried. Consequently the concentration of these metals in the hollow cathode discharge in helium is very low; they react only as normal atoms or possibly in the case of gallium and thallium as atoms in the very low metastable $^2P_{\frac{1}{2}}$ state. The limit is clearly set in the case of excitation in helium by $M+G^+$ or $M'+G^+$. There are no resonance maxima in these cases because, although the process $M+G'$ must contribute to the excitation, the limit of this excitation falls where the spectral terms are not numerous enough nor close enough together to make such a maximum apparent.

In the case of aluminum in argon and neon a new effect enters. The limit here is obviously set by M^++G'. That is, metal ions are entering this discharge although the concentration of metal in these cases is still so small that metal ions are not to an appreciable extent current carriers, as does occur in cases to be mentioned later. The greater number of metal ions is here due probably to the heavier bombardment of the cathode by the heavier gas particles. A similar effect appears in the vacuum spark where increased voltage on the spark giving heavier bombardment of the electrodes brings higher ionized atoms into the spark.

The limit of excitation for magnesium in helium and neon appears to be set respectively by the reactions $M'+G'$ and $M+G^+$, although these cases have perhaps not been investigated over a sufficiently wide spectral range for absolute certainty as to the limit.[2] In the neon the excitation goes somewhat (1/3 volt) above $M+G^+$ and a maximum corresponding to resonance with this process in the series 3^3D-m^3F is clearly seen. The energy for overshooting of the limit, $M+G^+$, probably comes from kinetic energy of the atoms. The process, M^++G', which sets the limit for Al+Ne probably does not occur here. It would call for excitation 13235 cm^{-1} beyond double ionization and as negative terms in Mg II are not possible and as there are no terms in Mg III as low as this, this process would involve freeing an electron with this surplus energy—a process which seems improbable. It will be seen that for magnesium and argon the limits of the five different processes are well separated and all positive. However, this case is not so favorable for observation as it seems for most of the limits are too low in the Mg II spectrum to allow maxima of excitation to be observed. It will

be noted from Table II that Frerichs observed excitation 10256 cm^{-1} above the highest limit. It is not clear how this can occur. A similar anomaly occurs with zinc in argon but in no other observed cases. It may be that here the reaction is with some high excited state of the metal atom but what state could occur with sufficient probability is not obvious.

Copper should offer an excellent opportunity to study excitation conditions in the rare gases since all the processes give rise to positive terms in Cu II. The copper spectrum is, however, unfortunately not completely analyzed and the combinations of the highest known terms lie largely in the extreme ultra violet. The highest term found by Kruger in helium, however, seems clearly to arise from $M'+G^+$. The process $M+G^+$ is responsible for a maximum of intensity found by Kruger for terms from 27–30000 cm^{-1}. Frerichs' work in neon did not lead to determination of any limit, but in argon the limit is set by M^++G' again, as with aluminum in neon and argon.[12]

Zinc, cadmium and mercury represent a different type of excitation condition. These metals have low boiling points and relatively high vapor pressure at the cathode temperature in the hollow cathode discharge. The ions of these metals enter the discharge in such concentrations as to carry a considerable part of the current. In fact in mercury the discharge may be operated without any rare gas using a carbon cathode and allowing the heat of the discharge to vaporize the mercury. Under such conditions we may expect that in all cases where the process M^++G' gives rise to actual terms that this reaction will set the limit to the excitation. This is indeed the case as will be seen by reference to Table II. In all these metals negative terms in the spectrum of the ion are possible and have been found so that the excitation has been traced to the highest limit permissable in helium. In zinc and cadmium the limit given in Table II is in fact exceeded by 3000 ν-units. This is possibly due to reaction with the higher metastable helium term (2^1S) which as pointed out previously would give excitation 6000 cm^{-1} higher than 2^3S which is given in the table. In the spectra of all these three metals some unclassified lines remain and more negative terms may be found to reach the limit M^++He' (2^1S). In helium with each of these metals there is also found maxima of excitation explainable as resulting from $M+G^+$ which appears in these cases to be more probable than $M'+G'$ no doubt because M' is so high in these metals that it is less likely to be excited strongly than in the case of copper or magnesium. The metals have not been studied in neon with the exception of zinc where, however, the spectral range covered by Frerichs was not sufficient to permit conclusions to be drawn. In argon, however, the limit is clearly set by M^++G' with cadium while with zinc, as mentioned above, even this limit which is the highest set by the simpler reactions, is exceeded by 25000 cm^{-1}. This, as in the case of Mg+A, does not appear susceptible to obvious explanation.

[12] Frerichs terms have been corrected to the true lowest term in Cu II not known at the time of his work.

In conclusion it may be said that the excitation of metallic spectra in the hollow cathode discharge in rare gases does not give results which are entirely predictable. In general with metals which do not sputter too freely nor have too high vapor pressures at the cathode temperatures, as Mg and Al, the reaction $M+G^+$ together with $M'+G'$ and $M'+G'$, if M' is low, will occur, and the highest of these will set the limit to the excitation if this does not call for non-existent negative terms. With such metals in neon or argon $M^+ + G'$ will in general occur due to the greater kinetic energy with which they bombard the cathode. With metals of high vapor pressure, as zinc, cadmium or mercury, $M^+ + G'$ will always set the limit if the terms called for are possible—i.e. not impossible negative terms.

While the limit of excitation will be set by whichever of the possible processes, as described above, possesses the greatest energy which the metal atom or ion can absorb, the processes leading to lower excitations will manifest themselves by maxima of excitation of the terms with which they are nearly in resonance, providing these excitation levels fall where the M^+ terms are close enough together for such maxima to be distinguishable.

For metals intermediate between the types above discussed it does not appear on the basis of present information possible to predict the excitation conditions. Whether or not metal ions will play a conspicuous part in the excitation will apparently depend too much on current density, cathode temperature and gas pressure in particular cases. Altering any of these may influence widely the character of the discharge. It would seem that by placing the metal in a carbon cathode whose temperature could be controlled by the discharge current density or by external heating, it should be possible to pass at will, by varying the vapor pressure of the metal and the gas pressure from the case of low vapor pressure with $M+G^+$ as limit to that of high vapor pressure with $M^+ + G'$ as limit. A complete theory of the discharge under all conditions and for all gases and metals is not yet possible.

ANALYTIC ATOMIC WAVE FUNCTIONS

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Abstract

The wave functions for the atoms Be, B, C, N, O, F, Ne, are written as simple analytic expressions with several parameters. The best values of these parameters are then determined by the variation method. In the final wave functions the effective quantum number is very nearly two, the radial node is so small as to have little effect upon the charge distribution, the coefficient in the exponential is related to an empirical "mean effective charge."

Introduction and Results

SEVERAL methods may be used to obtain approximate solutions of the wave equation for a many electron atom. Any one method cannot claim superiority in every respect. One naturally wants that type of solution which can be used to the best advantage. If he wants information derivable from a graphical $\psi\bar{\psi}$ distribution, then the Hartree[1] functions will be the best. In fact, the graphical method of integration, modified in the manner suggested by Slater[2] and Fock[3] to include resonance, will give the best approximation in which the total ψ is built from functions of only one electron, and in which magnetic forces are neglected.

If all questions could be answered by graphical functions without an undue amount of labor, we would not be justified in finding a less correct analytical ψ. But the integrals representing the mutual potential energy of two atoms are of a type which can be readily evaluated only when the wave functions are given by analytic expressions. Moreover, these integrals become increasingly laborious as the complexity of the atomic functions increases. Hence it is desirable to know the best possible functions which can be represented by simple analytic expressions.

Such atomic functions may be obtained starting from the hydrogenic solutions, exact when the interaction between the electrons is neglected, then partially taking care of this interaction by putting parameters into the function wherever flexibility may be obtained without increased complexity. This method has been used to obtain an approximate eigenfunction for Li by Guillemin and Zener.[4] In this paper the same method is applied to the normal states of the remaining elements in the first row of the periodic table.

[1] D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89–132 and 426–437 (1928).
[2] J. C. Slater, Phys. Rev. **35**, 210 (1930).
[3] V. Fock, Zeits. f. Physik **61**, 126, (1930).
[4] V. Guillemin Jr. and C. Zener, Zeits. f. Physik **61**, 199, (1930).

Slater[5] has shown how to write the wave function of a many electron system without the use of the group theory. Since the normal states here considered are states of highest multiplicity, the complete ψ may be written

$$\psi = \frac{1}{n!^{1/2}} \sum_P (-1)^{\sigma_P} P u(1/x_1) u(1/x_2) u(s/x_3) \cdots$$
$$\delta(-\tfrac{1}{2}/m_{s_1}) \delta(\tfrac{1}{2}/m_{s_2}) \delta(-\tfrac{1}{2}/m_{s_3}) \cdots$$

n is the number of electrons; P is an operator which permutes the electron numbers; σ_p is the order of the permutation P; $u(r/x_i)$ is a space coordinate function of the i^{th} electron in the r^{th} quantum state; $\delta(m_s/m_{s_i})$ is the spin function of the i^{th} electron in a state with spin component m_s. The summation is over all permutations.

We shall denote the states (100), (200), (21–1), (210), (211) by 1, s, a, b, c respectively. The normalised u's which have been generalised from their hydrogenic form are

$$u(1/x) = g_1 e^{-\gamma r}$$
$$u(s/x) = g_2 r^{n^*-1}(1 - \alpha r^{-1}) e^{-\delta r}$$
$$u(b/x) = g_3 \cos\theta r^{n^*-1} e^{-\delta r}$$
$$\binom{a}{c}/x = g_4 \sin\theta e^{\pm i\phi} r^{n^*-1} e^{-\delta r}$$

where r is written in units of a_H. In every atom the four parameters n^* α, γ, δ are to be determined by finding that set which makes

$$J = \frac{\sum_{m_{s_i}} \int \psi H \bar{\psi} d\tau}{\sum_{m_{s_i}} \int \psi \bar{\psi} d\tau} \tag{1}$$

a minimum. H is the Hamiltonian operator without magnetic interactions.

It is found that γ changes little from its value

$$\gamma = (N - 5/16)$$

in helium-like ions[6] (N equals atomic number). In Ne, where interpenetration is the largest, the change is from 9.69 to 9.64. This variation in γ does not affect the minimal value of δ in the significant figures used. It is of interest to note that the resonance of the two $2s$ electrons counterbalances their interpenetration to give a net negative shielding of the K shell.

The minimal values of the remaining parameters are in Table I.

The small effect of α upon the charge distribution is shown in Fig. 1 for Be. Here the quantity

[5] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[6] J. Frenkel, Einfuhrung in die Wellenmechanik, p. 291, Berlin, J. Springer, 1929.

$$D(x_1) = r_1^2 \sum_{m_{s_i}} \int \psi\bar{\psi} dx_2 dx_3 dx_4 \sin\theta_1 d\theta_1 d\phi_1$$

in Be is plotted with $\alpha = 0$, and its value for $\alpha = 0.15$ is indicated by crosses.

TABLE I.

	Li[a]	*Be*	*B*	*C*	*N*	*O*	*F*	*Ne*
$n^*(\pm.04)$	2.0	2.0	—	—	—	—	—	—
$\alpha(\pm.02)$	.18†	.15	.10	.07	.05	—	—	—
$\delta(\pm.01)$	.63	.96	1.26	1.59	1.92	2.24	2.56	2.88

[a] Taken from Guillemin and Zener, reference 4.
† ± 0.01
n^* has been varied only in Li and Be. Since in both atoms it has its hydrogenic value, it is to be expected to retain this value in the remaining atoms.

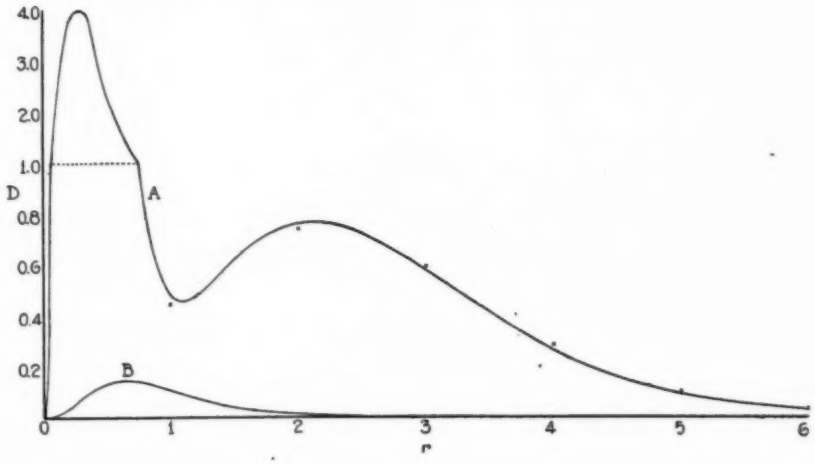

Fig 1.

A is electron density $\times r^2$ with $\alpha = 0$, crosses indicate values when $\alpha = 0.15$.
B is negative of resqnance charge density $\times r^2$

In the elements Be to Ne δ is $0.05 - 0.06$ less than the "mean effective charge" defined by

$$\bar{z} = n^*(\Sigma\epsilon_i/n)^{1/2}$$

in which $n^* = 2$, n is the number of electrons in the L shell, and the ϵ_i are the successive ionization potentials of the L shell expressed in E_H units. It is of interest to have a table of $\bar{z}$ for all the ions, as this relation will probably hold for the stripped atoms as well as for the neutral atoms. These are given in Table II. The $\bar{z}$'s of F and Ne are extrapolated, as well as of the negative ions.

When more than one electron is in the L shell, $\bar{z}$ is seen to increase in steps of unity as the nuclear charge is increased. The addition of each electron after the first $2p$ electron reduces $\bar{z}$ by 0.35.

TABLE II. $\bar{z}$ *of atoms and ions in first row. Numbers in parenthesis are ionization potentials.*[**]

No. of electrons in L shell	1	2	3	4	5	6	7	8
Li	1.260 (.3970)	1.02						
Be	2.316 (1.341)	2.02 (.702)						
B	3.342 (2.793)	3.02 (1.79)	2.63 (.612)	2.28				
C	4.358 (4.747)	4.02 (3.36)	3.63 (1.795)	3.28 (.829)	2.93			
N	5.366 (7.198)	5.02 (5.40)*	4.63 (3.49)	4.28 (2.18)	3.93 (1.97)	3.58		
O	6.372 (10.15)	6.02 (7.97)*	5.63 (5.69)	5.28 (4.05)	4.93 (2.59)	4.58 (1.001)	4.23	
F	7.376	7.02	6.63	6.28	5.93	5.58	5.23	4.88
Ne	8.376	8.02	7.63	7.28	6.93	6.58	6.23	5.88

* Exrapolated potetntials
** R. A. Millikan and I. S. Bowen, Proc. Nat. Acad. **13**, 531, (1927)

INTEGRATION OF J

Upon the introduction of

$$H = \sum h_i(x_i) + \sum 2/r_{ij}$$
$$h_i = -\Delta_i + 2N/r_i \tag{2}$$

into (1) we see that J can be reduced to a function of the integrals

$$g = \int u(1/x)u(s/x)dx$$
$$h_n{}^m = \int u(m/x)hu(n/x)dx \tag{3}$$
$$K_{nq}{}^{mp} = \int u(m/x_1)u(n/x_1)\frac{2}{r_{12}}u(p/x_2)u(q/x_2).$$

To facilitate this reduction we define

$$U(P) = PU(1) = Pu(1/x_1)u(1/x_2)u(s/x_3)\cdots$$
$$\Delta(P) = P\Delta(1) = P\delta(-\tfrac{1}{2}/m_{s_1})\delta(\tfrac{1}{2}/m_{s_2})\delta(-\tfrac{1}{2}/m_{s_3})\cdots$$
$$D(P', P'') = \sum_{m_{s_i}} \Delta(P')\Delta(P'').$$

The numerator of (1) becomes

$$\frac{1}{n!}\sum_{m_{s_i}}\int\left\{\sum_{P'}(-1)^{\sigma_{P'}}P'U(1)\Delta(1)\right\}\cdot H\cdot\left\{\sum_{P''}(-1)^{\sigma_{P''}}P''U(1)\Delta(1)\right\}d\tau$$

$$=\frac{1}{n!}\sum_{P'}P'\sum_{m_{s_i}}\int U(1)\Delta(1)H\sum_{P}(-1)^{\sigma_P}PU(1)\Delta(1)d\tau$$

where $P'\cdot P=P''$, and hence $(-1)^{\sigma_{P'}+\sigma_{P''}}=(-1)^{\sigma_P}$.

Since the integrals and summation are independent of P', and since there are in all $n!$ permutations, the numerator reduces to

$$\int U(1)H\sum_{P}(-1)^{\sigma_P}D(1,P)PU(1)d\tau. \tag{4}$$

Similarly the denominator becomes

$$\int U(1)\sum_{P}(-1)^{\sigma_P}D(1,P)PU(1)d\tau.$$

Observing that $D(1, P)$ vanishes whenever two electrons with opposite spin are permuted, and that $u(1/x)$ is orthogonal to $u(a/x)$, $u(b/x)$ and $u(c/x)$, the denominators for Be and the succeeding atoms reduce to

$$\begin{aligned}&\int U(1)[1-(13)][1-(24)]U(1)d\tau\\&=\left(\int u(1/x_1)u(s/x_3)[1-(13)]u(1/x_1)u(s/x_3)dx_1dx_3\right)^2 \qquad (5)\\&=(1-g^2)^2.\end{aligned}$$

Here the operator interchanging electrons i and j has been denoted by (ij).

Putting (2) into (4) and using (5) gives the J's for the various atoms in terms of the integrals (3).

$$\begin{aligned}J_{Be} &= 2(h_1^1+h_s^s-2gh_s^1)/(1-g^2)+[K_{11}^{11}+K_{ss}^{ss}+2(2-g^2)K_{1s}^{1s}\\&\quad+(-2+6g^2)K_{ss}^{11}-4g(K_{1s}^{11}+K_{ss}^{1s})]/(1-g^2)^2\\J_B &= J_{Be}+h_a^a+[2K_{1a}^{1a}+2K_{sa}^{sa}-K_{aa}^{11}-K_{aa}^{ss}+2gK_{aa}^{1s}-4gK_{sa}^{1a}]/(1-g^2)\\J_c{}^3P &= 2J_B-J_{Be}+K_{ab}^{ab}-K_{bb}^{aa}\\J_N{}^4S &= 3J_B-2J_{Be}+2K_{ab}^{ab}-2K_{bb}^{aa}+K_{aa}^{aa}-K_{cc}^{aa}\\J_0{}^3P &= 4J_B-3J_{Be}+3K_{ab}^{ab}-2K_{bb}^{aa}+3K_{aa}^{aa}-K_{cc}^{aa}\\J_F{}^2P &= 5J_B-4J_{Be}+4K_{ab}^{ab}-2K_{bb}^{aa}+6K_{aa}^{aa}-2K_{cc}^{aa}\\J_{Ne}{}^1S &= 6J_B-5J_{Be}+8K_{ab}^{ab}-4K_{bb}^{aa}+6K_{aa}^{aa}-2K_{cc}^{aa}+K_{bb}^{bb}\end{aligned}$$

These expressions are the same as those given by Peierls[7] except that he has assumed $g=0$ and the equivalence of such integrals as K_{ab}^{ab} and K_{aa}^{aa}

Comparison of Energy Values

A comparison of the observed energy required to strip the L shell in Be, B, C with the calculated energy of the L shell gives a measure of the approp-

[7] R. Peierls. Zeits. f. Physik **55**, 738 (1929).

riateness of our functions in representing the actual eigenfunctions. This is given in Table III.

TABLE III. *Energy of L shell in volts.*

	Li*	Be	B	C
obs.	5.37	27.64	70.3	145.2
calc.	5.32	25.86	68.1	142.7
error	.05	1.8	2.2	2.5

* Taken from Guillemin and Zener, reference 4.

The calculated energy of the L shell is to be defined as the minimum of J minus the calculated energy of the unperturbed K shell[8]

$$E_K = -2(N - 5/16)^2. \tag{6}$$

The calculated energies of the remaining L shells are 258.3, 417.8, 633.5, 919.0 volts for N, O, F, Ne, respectively. A comparison with extrapolated values of the empirical energies gives decidedly worse agreement.

It was found that in a series of ions, such as Be, B^+, C^{++}, the discrepancy remains nearly constant between the empirical energies and those calculated from simple analytic functions. The helium series is of particular interest, where the energy[6] is given by the function

$$\psi = g_A e^{-(N-5/16)(r_1+r_2)}.$$

TABLE IV. *Energy of helium-like ions (volts.)*

	He	Li	Be
obs	78.59	197.05[9]	369.58[9]
Calc.	77.05	195.44	367.94
Error	1.54	1.61	1.64

The multiplet separations have been calculated by the method given by Slater.[5] They are from 1.5 to 2 times too large.

SUMMARY

Approximate solutions for the normal states of the elements in the first row have been calculated. The parameters in these solutions were either found to have nearly fixed values ($n^*=2$, $\gamma=N-5/16$, $\alpha\backsimeq 0$), or values nearly equal to empirical quantities ($\delta=\bar{z}$). It is to be expected that these parameters will behave similarly in the ions of these atoms. By means of a table which is given for the $\bar{z}$ of the various ions, one may thus write an approximate solution for all the ions, positive and negative, of the atoms in the first row. α will, however, become of increasing importance as the positive charge of the ions increases.

The writer wishes to express his gratitude to Professors Slater and Hartree for illuminating discussions. He also wishes to thank Harvard University for a Sheldon Fellowship which has enabled him to complete this work.

[8] J. Frenkel, reference 6.

[9] B. Elden and A. Ericson, Nature **124**, 688 (1929).

ATOMIC SHIELDING CONSTANTS

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Abstract

In analogy with the method of Zener for the atoms from Li to F, simple rules are set up giving approximate analytic atomic wave functions for all the atoms, in any stage of ionization. These are applied to x-ray levels, sizes of atoms and ions, diamagnetic susceptibility, etc. In connection with ferromagnetism it is shown that if this really depends on the existence of incomplete shells within the atoms, rather far apart in the crystal, then the metals most likely to show it would be Fe, Co, Ni, and alloys of Mn and Cu (Heusler alloys).

IT IS often extremely useful to have simple approximations to the wave functions and energy levels of atoms and ions. Zener[1] has derived such functions for the atoms up to F, fixing the values of his parameters by variation methods. In the present paper, the functions are tentatively extended to the other atoms. The shielding constants and other parameters are not fixed by variation methods, but adjusted merely to get agreement with empirical values of stripped atom and x-ray energy levels, sizes, etc., so that the values do not have the certainty of Zener's calculations. It is to be hoped that eventually a variation calculation can be made here too; but we may anticipate that the figures given in this paper will be substantially verified, and in the meantime, an approximate set of functions is much better than none. The principal set of shielding constants which now exists is that of Pauling,[2] and it is believed that the present set is simpler, more general, and more accurate. The density functions derived from the present shielding constants agree fairly well with those found by Hartree's method, in cases where that has been carried out.

The Wave Functions

The nodes in the wave function are found by Zener to be unimportant, and a glance at Hartree's distribution, say for Rb^+, shows that they come much nearer the nucleus than for hydrogen wave functions, and are therefore less important. Consequently we neglect them entirely, taking as the radial part of the wave function of one electron simply

$$r^{n^*-1}e^{-((Z-s)/n^*r)},$$

the asymptotic form at large distances for a hydrogen-like wave function of quantum number n^* in the field of a nuclear charge $(Z-s)$. Here Z is sup-

[1] C. Zener, Phys. Rev. **36**, 51 (1930); Guillemin and Zener, Zeits. f. Physik **61**, 199 (1930).

[2] Linus Pauling, Proc. Roy. Soc. **A114**, 181 (1927).

posed to be the actual charge on the nucleus, and s is a screening constant. We assign values of n^*, the effective quantum number, and $Z-s$, by simple rules, to the electrons in each shell in each atom or ion, and so have a complete set of one-electron wave functions. The method of combining such one-electron wave functions into functions for the whole atom has been described elsewhere.[3]

The values of n^* and $(Z-s)$ are given by the following rules:

(1) n^* is assigned by the following table, in terms of the real principal quantum number n:

for $n=1, 2, 3, 4, 5, 6$
$n^*=1, 2, 3, 3.7, 4.0, 4.2$

(2) For determining $Z-s$, the electrons are divided into the following groups, each having a different shielding constant: $1s$; $2s, p$; $3s, p$; $3d$; $4s, p$; $4d$; $4f$; $5s, p$; $5d$; etc. That is, the s and p of a given n are grouped together (as Zener has done), but the d and f are separated. The shells are considered to be arranged from inside out in the order named.

(3) The shielding constant s is formed, for any group of electrons, from the following contributions:

(a) Nothing from any shell outside the one considered.

(b) An amount 0.35 from each other electron in the group considered (except in the $1s$ group, where 0.30 is used instead).

(c) If the shell considered is an s, p shell, an amount 0.85 from each electron with total quantum number less by one, and an amount 1.00 from each electron still further in; but if the shell is a d or f, an amount 1.00 from every electron inside it.

As a first example, we take C, $Z=6$. Here we have two $1s$ electrons, four $2s, p$ electrons. For effective nuclear charge, $Z-s$, we have

$1s$: $6-0.30=5.70$ (Zener has 5.6875)
$2s, p$: $6-3(0.35)-2(0.85)=3.25$ (Zener has $1.59\times 2=3.18$)

As a second example, we take Fe, $Z=26$. There are two $(1s)$'s, eight $(2s, p)$, eight $(3s, p)$, six $(3d)$, two $(4s)$. The effective nuclear charges are

$1s$: $26-0.30=25.70$
$2s, p$: $26-7(0.35)-2(0.85)=21.85$
$3s, p$: $26-7(0.35)-8(0.85)-2(1.00)=14.75$
$3d$: $26-5(0.35)-18(1.00)=6.25$
$4s$: $26-1(0.35)-14(0.85)-10(1.00)=3.75$.

Finally we take Fe, lacking a K electron, so that there is only one $(1s)$, but otherwise it is as before. Then

$1s$: 26.00
$2s, p$: $26-7(0.35)-1(0.85)=22.70$
$3s, p$: $26-7(0.35)-8(0.85)-1(1.00)=15.75$
$3d$: $26-5(0.35)-17(1.00)=7.25$
$4s$: $26-1(0.35)-14(0.85)-9(1.00)=4.75$.

[3] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

The Energy Values

The total energy of an atom or ion—the negative of the energy required to remove all electrons from the nucleus to an infinite distance—is found by Zener to be accurately given by the sum of the quantities $-((Z-s)/n^*)^2$ for all electrons of the atom (This is the significance of his connection of the shielding constant with the empirical "mean effective charge"). This is very reasonable. If we take as an atomic wave function a product of one-electron wave functions of our type, for each electron, then allow the energy operator to act on it, the result will consist of several parts, as one can readily verify: (1) the sum of $-((Z-s)/n^*)^2$ for each electron, times the function, coming from the second derivative in the Laplacian operator; (2) terms in $1/r$, and higher powers, times the function, coming from the Laplacian; (3) terms in $1/r$, times the function, coming from the potential energy. For the correct wave function, (2) and (3) will cancel each other, leaving just terms (1), a constant times the function, so that Schrödinger's equation will be satisfied. It seems very reasonable that, in a wave function which is a good approximation, this will be nearly the case too. But this leaves as the energy just the sum which we have mentioned. We therefore take that as giving the energy of an atom or ion, saving ourselves by this simple rule from the necessity of computing the energy by the usual method of integrating H. This of course gives the energy in terms of the Rydberg energy.

As a first example, we take the energy required to remove all the L electrons from C. We have

normal atom: $-2(5.70)^2-4(3.25/2)^2=-64.98-10.56=-75.54$
atom with L electrons stripped off: $-2(5.70)^2=-64.98$
Difference = energy of removal = $10.56=10.56\times13.56$ volts
$=143.2$ volts (correct, 145.2; Zener has 142.7)

As a second example, we take the energy required to remove any electron from the Fe atom, We have

normal atom: $-2(25.70)^2-8(21.85/2)^2-8(14.75/3)^2-6(6.25/3)^2-2(3.75/3.7)^2=-2497.2$

atom lacking one $1s$ electron: $-1(26.00)^2-8(22.70/2)^2-8(15.75/3)^2-6(7.25/3)^2-2(4.75/3.7)^2=-1964.6$. Difference $=532.6$; observed K absorption limit $=524.0$

atom lacking one $2s$, p electron: $-2(25.70)^2-7(22.20/2)^2-8(15.60/3)^2-6(7.25/3)^2-2(4.75/3.7)^2=-2437.7$. Difference $=59.4$; observed L absorption limits, $L_{11}=61.9$, $L_{21}=53.4$, $L_{22}=52.4$

atom lacking one $3s$, p electron: -2491.1; difference $=6.1$; observed $M_{11}=7.07$; M_{21}, $M_{22}=4.2$

atom lacking one $3d$ electron: 2496.4; difference $=0.8$; observed energy of removal of $3d$ electron from Fe atom, by Moseley law in optical spectra, 0.8

atom lacking one $4s$ electron: 2496.3; difference $=0.9$; observed energy of removal of $4s$ electron $=0.58$

It is interesting to notice in this example how the so-called "outer shielding" of the x-ray terms comes about, by the decrease of the shielding constants of the outer electrons when an inner electron is removed. It is also interesting to see how this rearrangement of shielding constants brings it about that the $3d$ electrons, although much further in than the $4s$, still require about the same energy for their removal.

As a final example, we take the ionization potential of the alkalies:

normal Li: energy of K shell $-(1.30/2)^2$ = energy of K shell -0.423
ionized Li: energy of K shell; difference $=0.423$; observed ionization potential $=0.397$.

We observe that we can get these ionization potentials directly, without considering the inner shells. Thus we have for the ionization potentials:

Na $(2.20/3\ )^2=0.537$, observed $=0.378$
K $(2.20/3.7)^2=0.354$, observed $=0.319$
Rb $(2.20/4.0)^2=0.302$, observed $=0.307$
Cs $(2.20/4.2)^2=0.274$, observed $=0.287$

The examples which we have worked out are a fair sample of the energies obtained in general from the scheme; one sees that they are qualitatively accurate, though by no means to be trusted in detail. The principal criterion used in setting up the rules for the shielding constants has been to make the energy check fairly well with experiment.

Sizes of Atoms and Ions

The maximum of the radial charge density for one of our shells comes, as we immediately find by differentiation, at $(n^*)^2/(Z-s)$. Thus our shielding constants permit us to compute the sizes of atoms and ions. For example, the radius, as defined in this way, of the outer, $4s$ shell of Fe is $(3.7)^2/3.75 = 3.65 = 1.95$ Angstroms. The radii of the outer shells, defined in this way, can be brought into interesting connection with the internuclear distances in valence compounds and in metals, in which the substances exist in the atomic state. For binding, we should expect that the electrons forming the bond would wish to have the maximum possible overlapping, which would come if the internuclear distance were the sum of the radii so defined, so that the maxima of density lay together. As a matter of fact, this is closely the case, when the valence electrons are p electrons; but when both valences are s electrons, the distances are smaller, about 2/3 of this. In any case, the correlation is quite good, and should be useful in predicting approximate internuclear distances where they are not known. We give, in Table I, the atomic radii so derived, and in Table II a number of internuclear distances, as observed in band spectra and crystals, together with the sum of the theoretical radii for comparison, and the ratio of the two. These ratios are, as we stated, about 1 when one or both valences are p electrons, but about 2/3 when both are s electrons. In a few cases, such as the hydrogen halides, where one might suppose the substances to be ionic rather than valence

compounds, the excellent agreement with our rule gives us confidence that the valence bond essentially describes the situation.

TABLE I. *Atomic radii (Angstroms).*

(These radii are the radii of the values for maximum radial density in the charge distributions of the outer shells of the neutral atoms, computed from the effective quantum numbers and effective nuclear charges by the formula $(n^*)^2/(Z-s)$.

H	0.53								
Li	1.63	Na	2.17	K	3.32	Rb	3.86	Cs	4.25
Be	1.09	Mg	1.68	Ca	2.56	Sr	3.00	Ba	3.30
B	.82	Al	1.37	Sc	2.43	Y	2.84	La	3.12
C	.65	Si	1.15	Ti	2.32	Zr	2.71	—	—
N	.55	P	1.00	V	2.22	Nb	2.60	Ta	2.86
O	.47	S	.88	Cr	2.12	Mo	2.48	W	2.73
F	.41	Cl	.78	Mn	2.02		2.36		2.60
				Fe	1.95	Ru	2.28	Os	2.51
				Co	1.87	Rh	2.18	Ir	2.40
				Ni	1.80	Pd	2.10	Pt	2.31
				Cu	1.73	Ag	2.02	Au	2.22
				Zn	1.67	Cd	1.95	Hg	2.15
				Ga	1.46	In	1.71	Tl	1.88
				Ge	1.29	Sn	1.51	Pb	1.66
				As	1.16	Sb	1.35	Bi	1.48
				Se	1.05	Te	1.22		
				Br	.96	I	1.12		

TABLE II. *Internuclear distances in valence compounds (Angstroms).*

(Observed internuclear distances, observed from band spectra or crystal structure. Band spectrum data are taken from Report of National Research Council on Molecular Spectra in Gases, pp. 222–232, except for the following: BO, Jenkins, Proc. Nat. Acad. Sci. **13**, 496, (1927); NO, Guillery, Zeits. f. Physik **42**, 121 (1927), recalculated by Birge; OH, Report as above, but corrected by Birge; H_2O, Debye, Polare Molekeln, Hirzel, 1929, p. 85; HI, Czerny, Zeits. f. Physik **44**, 236 (1927), calculated by Birge; H_2, Birge, Proc. Nat. Acad. Sci. **14**, 12 (1928); Na_2, Loomis, Phys. Rev. **32**, 223 (1928); MgH, Watson and Rudnick, Phys. Rev. **29**, 413 (1927). Data on crystal structure are from Landolt-Börnstein, Tables, 5th Ed., Ergänzungsband.

The columns are as follows: (1) substances; (2) observed internuclear distances; (3) sum of atomic radii for outer shell, as given in Table I; (4) ratio of observed distance to sum of radii; (5) sum of atomic radii for inner incompleted shell, in substances which might be ferromagnetic; (6) ratio of observed distance to sum of radii of inner shells. Substances are divided into four classes: (a), molecules with one or both valences p electrons; (b) molecules with both valences s electrons; (c) crystals with one or both valences p electrons; (d) crystals with both valences s electrons.)

Part (a): Molecules with one or both valences p electrons.

(1) Substance	(2) Distance observed	(3) Sum of radii	(4) Ratio obs/calc
BO	1.21	1.29	0.94
CH	1.13	1.18	.96
CN	1.17	1.20	.98
CO	1.15	1.12	1.02
NO	1.15	1.02	1.12
N_2	1.21	1.10	1.10
O_2	1.20	.94	1.28
OH	.98	1.00	.98
H_2O	1.07	1.00	1.07
AlH	1.66	1.90	.87
AlO	1.62	1.84	.88
SiN	1.56	1.70	.92
I_2	2.66	2.24	1.19
HF	.92	.94	.98
HCl	1.28	1.31	.98
HBr	1.42	1.49	.95
HI	1.62	1.65	.98

Part (b): Molecules with both valences *s* electrons.

(1) Substance	(2) Distance observed	(3) Sum of radii	(4) Ratio obs/calc
H_2	.76	1.06	.71
Na_2	3.08	4.34	.71
CuH	1.47	2.26	.65
AgH	1.63	2.55	.64
AuH	1.54	2.75	.56
MgH	1.74	2.21	.79
CaH	2.01	3.09	.65
ZnH	1.61	2.20	.73
CdH	1.78	2.48	.72
HgH	1.76	2.68	.66

Part (c): Crystals with one or both valences *p* electrons.

(1) Substance	(2) Distance observed	(3) Sum of radii	(4) Ratio obs/calc
C (diamond)	1.54	1.30	1.18
(graphite)	1.43	1.30	1.10
(ethane C−C)	1.55	1.30	1.19
C−N (KCN)	1.15	1.20	.96
Al	2.86	2.74	1.04
Si	2.35	2.30	1.02
Ge	2.44	2.58	.95
As	2.51	2.32	1.08
Se	2.35	2.10	1.12
In	3.24	3.42	.95
Sn (diamond lattice)	2.80	3.02	.93
Sn (white)	3.02	3.02	1.00
Sb	2.87	2.70	1.06
Te	2.87	2.44	1.18
Tl	3.36	3.76	.89
Pb	3.48	3.32	1.05
Bi	3.10	2.96	1.04

Part (d): Crystals with both valences *s* electrons.

(1) Substance	(2) Distance observed	(3) Sum of radii	(4) Ratio obs/calc	(5) Sum of radii inner shell	(6) Ratio obs/calc inner shell
Li	3.03	3.26	.93		
Be	2.23	2.18	1.02		
Na	3.72	4.34	.86		
Mg	3.22	3.36	.96		
K	4.50	6.64	.68		
Ca	4.97	5.12	.78		
Ti	2.93	4.64	.63	2.62	1.12
V	2.63	4.44	.59	2.22	1.18
Cr	2.51	4.24	.59	1.93	1.30
Mn	2.52	4.04	.62	1.71	1.47
Fe	2.50	3.90	.64	1.53	1.63
Co	2.51	3.74	.67	1.38	1.82
Ni	2.50	3.60	.69	1.27	1.97
Cu	2.54	3.46	.73		
Zn	2.67	3.34	.80		
Zr	3.18	5.43	.59	4.00	.79
Mo	2.72	4.96	.55	2.94	.92
Ru	2.64	4.56	.58	2.33	1.13
Rh	2.70	4.36	.62	2.11	1.28
Pd	2.73	4.20	.65	1.93	1.41

Part (d): Crystals with both valences *s* electrons—*Continued.*

(1) Substance	(2) Distance observed	(3) Sum of radii	(4) Ratio obs/calc	(5) Sum of radii inner shell	(6) Ratio obs/calc inner shell
Ag	2.88	4.04	.71		
Cd	2.96	3.90	.76		
Ta	2.83	5.72	.50	3.95	.72
W	2.73	5.66	.48	3.44	.79
Os	2.71	5.02	.54	2.72	1.02
Ir	2.70	4.80	.56	2.47	1.09
Pt	2.77	4.62	.60	2.25	1.23
Au	2.87	4.44	.65		

In studying valence, we are interested in the size of the outer shell, but for ferromagnetism the essential, as the writer has shown in an earlier paper,[4] is the existence of an inner shell in process of formation, small enough so that the distance of separation is relatively great compared with the size of the shell. To see what metals should show ferromagnetism, if this idea is correct, we also give in Table II the radii for the *d* shells in process of formation in the transition groups, and the ratio of internuclear distance to twice this radius. This ratio is greater for Fe, Co, and Ni than for any other element, so that these would be most likely to be ferromagnetic. We might suppose that as two such shells were moved apart, the interaction was nonferromagnetic (the terms of lowest multiplicity lying lowest) out to about 1.55 times the sum of the radii; there the interaction would change sign, passing through a critical region (suggesting the fact that Mn sometimes shows magnetic properties, usually not). The first element beyond the critical region, Fe, would show the greatest ferromagnetism. As the internuclear distance still further increased, the exponential dropping off of the wave function would make the interaction less, resulting in weaker effects in Co and Ni. These conclusions are made much more reasonable by considering the Heusler alloys. Here Cu takes the place of Mn in an alloy with Al or other substance, and the alloy is almost as ferromagnetic as Fe. Now if Cu can replace Mn, it is presumably in a form with two 4*s* electrons, nine 3*d*'s so that it has an open shell of *d* electrons, which is even smaller than for Ni (radius = 1.17/2A). This very small radius, added to the large radius of Mn, gives a sum of 1.44A, and a ratio intermediate between Fe and Co, suggesting a strong ferromagnetism, although Mn by itself is too big, Cu too small (and in ordinary Cu undoubtedly the 3*d* shell is closed anyway) to show ferromagnetic properties.

In ionic compounds, the atoms exist as ions, which have closed shells; and the interionic forces are repulsions (except for the electrostatic attractions), and account for the hardness and impenetrability of the structures. These repulsions become large, as has often been shown, as soon as the outer shells begin to overlap, and the internuclear distances in ionic crystals should be the sums of radii representing, not the radius of maximum density in the shell, but a considerably larger radius at which the charge just begins to become

[4] J. C. Slater, Phys. Rev. **35**, 509 (1930).

appreciable. It appears that the appropriate radius is roughly one at which the radial density becomes 10 percent of its maximum value. By solving the problem numerically, we find that for the density function we have used, this radius is a numerical factor times the radius of maximum density, this factor being 3.38 for $n^*=1$, 2.49 for $n^*=2$, 2.25 for $n^*=3$, 2.01 for $n^*=3.7$, 1.96 for $n^*=4.0$. Thus, finding the radius of maximum density, now for the ion rather than for the atom, and using these factors to get radii of 10 percent density, we get the ionic radii given in Table III. They should be compared with the ionic radii of Wasastjerna, which are to be added to give grating spaces, and which are also tabulated. It is seen that the agreement in general is decidedly good. This renders it highly probable that the atoms really exist in these compounds as ions, as has been supposed. Computed values are included for the inert gases, and these should be the radii of these gases, as derived in the kinetic theory. The latter of course vary over a considerable range, but our values seem to lie well within this range in each case. For example, for He, Jeans in his "Dynamical Theory of Gases" gives values from 0.99A to 1.10A, as determined by various methods; our value is 1.05A.

TABLE III. *Ionic radii* (*Angstroms*).

(Observed radii as given by Wasastjerna; see for instance W. L. Bragg, Phil. Mag. **2**, 258 (1926); the sum of these radii gives the interionic distance in ionic crystals. Calculated values are for radius where density is 10% of its maximum value. This equals constant times $(n^*)^2/(Z-s)$, where the constant equals 3.38 for $n^*=1$, 2.49 for $n^*=2$, 2.25 for $n^*=3$, 2.01 for $n^*=3.7$, 1.96 for $n^*=4.0$)

Ion	Observed	Calculated	Ion	Observed	Calculated
H^-		2.57	$Se^=$		2.34
He		1.05	Br^-	1.92	2.02
Li^+	0.76	.67	Kr		1.77
Be^{++}	(.3)	.49	Rb^+	1.50	1.58
			Sr^{++}	1.20	1.43
$O^=$	1.32	1.37			
F^-	1.33	1.09	$Te^=$		2.66
Ne		.91	I^-	2.19	2.30
Na^+	1.01	.77	Xe		2.02
Mg^{++}	.75	.67	Cs^+	1.75	1.80
Al^{+++}	(.55)	.60	Ba^{++}	1.40	1.62
Si^{4+}	(.3)	.54			
$S^=$	1.69	2.16			
Cl^-	1.72	1.79			
A		1.52			
K^+	1.30	1.33			
Ca^{++}	1.02	1.17			

We can get a valuable check on the size of atoms by using the diamagnetic susceptibility, which is proportional to the mean value of Σr^2. From our wave functions, by integration we find this quantity for one of the electrons to be $(n^*)^2\,(n^*+1/2)\,(n^*+1)/(Z-s)^2$. For the inert gases, we have the following values:

	computed	observed
He	2.07	2.34
Ne	7.08	8.31
A	23.37	22.6

A SEARCH FOR THE SOURCE OF DIELECTRIC POLARIZATION

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Abstract

A brief discussion is given of the work of Hengstenberg on the same subject. A theory of the distortion of a polar cubic lattice by electric stress is derived with the method suggested by Richardson for calculating electric stress on the ions, and the frequency of residual rays for determining the restraining forces. The effect of the distortion on intensity of x-ray reflection is then calculated in the usual manner. Measurements of change in intensity of reflected x-rays were made with a precision of about 0.1 percent in the 4th and 5th orders for NaCl and the 5th order for KCl using gradients up to 700 kv/cm. It is concluded that the effect is probably not as large as predicted by Hengstenberg, i.e., the polarization is probably not due to motion of the ions as units. The precision of the experiments was not high enough to determine whether the theory derived here is correct.

IF A polar crystal is subjected to electric stress the positive and negative ions might be expected to be displaced in opposite directions. The distorted lattice would then reflect x-rays less intensely than before distortion. J. Hengstenberg[1] has derived a theory of this effect based on the assumption that the total polarization is due to the displacement of the ions as units. This assumption seems hardly justified since the polarization effects exhibited by nonpolar substances are of the same order of magnitude as those of polar substances. However Hengstenberg has tested his theory for KCl and found the experimental results in agreement.

A calculation of the electrostatic force due to an external field on an ion in a crystal of this type can be made following the method suggested by Richardson.[2] By considering the forces due to the condenser charge, the polarization charge, and the doublets in the neighborhood of the ion, the following equation is obtained:

$$f_e = \frac{K+2}{3K} Ee \text{ dynes} \qquad (1)$$

where K is the dielectric constant, E the field in e.s.u. per cm, and e is the electronic charge in e. s. u.

The binding forces on the atoms in a crystal can be calculated if we assume their resonance frequency to be that of the residual rays. The differential equation is:

$$m\ddot{x} + qx = 0$$

where m is the mass of the atom and q the restoring force per unit displacement.

[1] J. Hengstenberg, Zeits. f. Phys. **58**, 345 (1929).
[2] O. W. Richardson, Electron Theory of Matter p. 71 *et seq.*

A solution of the equation is:

$$x = A \cos (pt + \theta)$$

where

$$p = (q/m)^{1/2} = 2\pi\nu = 2\pi c/\lambda$$

λ being the resonance wave-length and c the velocity of light.
Then

$$q = 4\pi^2 c^2 m/\lambda^2 \text{ dynes/cm}$$

or for a displacement of δ cm

$$f_\delta = 4\pi^2 c^2 m\delta/\lambda^2. \tag{2}$$

If the binding forces for $\lambda = \infty$ are not substantially different from those for the wave-lengths of the residual rays then $f_\delta = f_e$ or combining Eqs. (1) and (2)

$$\frac{K+2}{3K} Ee = 4\pi^2 c^2 m\delta/\lambda^2$$

whence

$$\delta = \frac{\lambda^2}{4\pi^2 c^2 m} \frac{K+2}{3K} eE \tag{3}$$

If the lattice is distorted by moving alternate atoms in opposite directions in a cubic crystal, the intensity of the x-rays reflected may be shown to be:[3]

$$I_\delta = I_0 \cos^2 2\pi n\delta/D$$

where I_δ = intensity from distorted lattice

I_0 = intensity from undistorted lattice
n = order of reflection
δ = distance through which each atom is moved
D = distance between adjacent atomic layers.

The fractional change in intensity due to distortion is then:

$$\frac{\Delta I}{I} = \frac{I_0 - I_\delta}{I_0} = 1 - \cos^2 2\pi n\delta/D = \sin^2 2\pi n\delta/D$$

and for small values of δ

$$\frac{\Delta I}{I} = (2\pi n\delta/D)^2. \tag{4}$$

Combining Eqs. (3) and (4)

$$\frac{\Delta I}{I} = \left[\frac{(K+2)\lambda^2 ne}{6\pi K mc^2 D}\right]^2 E^2.$$

[3] cf. A. H. Compton, X-rays and Electrons Chap. V.

With the values $e=4.77\times10^{-10}$, $c=3\times10^{10}$ and for NaCl

$$K=6.12$$
$$\lambda=52\times10^{-4}\text{ cm}$$
$$D=2.81\times10^{-8}\text{ cm}$$
$$m=23.00+35.46/2\times6.06\times10^{23}=4.84\times10^{-23}\text{ grams}$$

and for KCl

$$K=5.03$$
$$\lambda=63.4\times10^{-4}\text{ cm}$$
$$D=3.14\times10^{-8}\text{ cm}$$
$$m=39.10+35.46/2\times6.06\times10^{23}=6.18\times10^{-23}\text{ grams.}$$

For the 4th order NaCl $\Delta I/I=0.89\times10^{-11}\,E^2$.

For the 5th order NaCl $\Delta I/I=1.40\times10^{-11}\,E^2$.

For the 5th order KCl $\Delta I/I=1.68\times10^{-11}\,E^2$.

These values are plotted in the dotted curves of figs. 3, 4 and 5. The corresponding values obtained from Hengstenberg's equations are represented by the dashed lines. The difference between these predictions would seem to be due to Hengstenberg's neglect of possible distortion of the ion under the influence of the applied electric field.

Experimental Arrangement

The source of x-rays was a water-cooled Coolidge molybdenum target tube immersed in oil and operated at from 30 to 45 ma. and 40 to 50 peak k. v. by a full wave rectifier. The crystals under test were mounted on the table of a spectrometer which also carried an arm for supporting the ionization chamber. The ionization currents were measured by means of a screen grid amplifier described in detail elsewhere,[4] the variations in the plate current being measured by a galvanometer. A record of the galvanometer deflection was traced photographically on bromide paper, which was drawn at a constant rate by a synchronous-motor-driven reduction gear.

The crystals were mounted in a manner essentially the same as that used by Hengstenberg. This consisted of splitting the crystal as thin as conveniently possible, then mounting by means of sealing wax over a hole of about 7 mm diameter in a glass plate. After mounting, the crystal can be reduced to the desired thickness by washing with water. The thickness of the crystals used ranged from about 0.25 to 0.40 mm, a rough measurement being made by means of a dial test indicator before use, and more exactly by micrometer calipers after puncture. A circular piece of very thin aluminum foil was cemented with shellac to each side of the crystal for applying the electric stress.

The source of voltage for the crystals consisted of a kenotron rectifier set with a condenser, and could supply up to 21 k.v. direct current. This source was connected to the back foil of the crystal through a resistance of several megohms, the foil on the reflecting side being grounded. The high

[4] R. D. Bennett, An Amplifier for Measuring Small Currents Rev. of Sci. Inst. in press.

voltage was switched on and off by means of a kenotron which when the filament was lighted served to ground the back surface of the crystal. The kenotron filament was switched by the same mechanism that moved the photographic paper, and an auxiliary light traced a record on the paper whenever the kenotron filament was lighted. The amplifier for the ionization

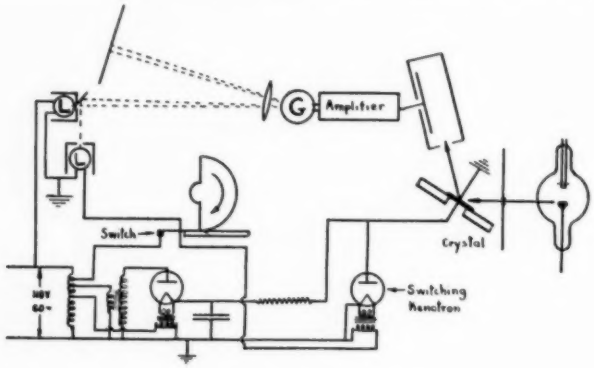

Fig. 1. Diagram of apparatus.

current was so sensitive to high frequency surges that this method of switching was necessary. For the same reason sources of sparking in the x-ray supply circuit had to be removed. Voltage on the crystal was measured by means of a spark gap. Fig. 1 is a diagram of the circuits.

The amplifier arrangement reads the ionization current directly, and the electrostatic capacity of the collector is so small that the ionization from the

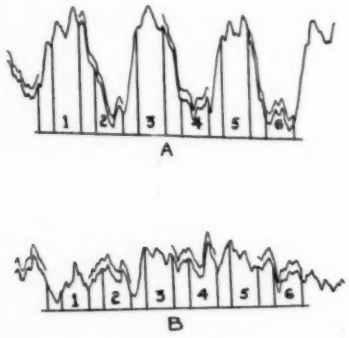

Fig. 2.

individual photoelectrons produces variations in the plate current. This makes the galvanometer trace a wavy line, the fluctuations being of the order of 1 percent in the arrangement used. Hence it was necessary, in order to measure to higher precision than 1 percent to take an average over a number of intervals. The method of analysis of the records is best shown by Fig. 2. The trace A is a calibration curve obtained by alternately inserting and removing a screen which absorbs a_0 percent of the x-ray beam. The sum of the areas 1, 3, 5 etc. is measured by means of a planimeter and an average area

s_0 found. From this is subtracted the average of the even areas s_e. Then $s_0 - s_e/a_0 = s_1$ gives the average area difference equivalent to 1 percent change in intensity. The curve B which is made with the field alternately on and off is then analysed in the same manner giving an average difference, say s_2. Then the ratio s_2/s_1 gives the fraction of 1 percent change due to the field. The precision of the result will be proportional to the square root of the num-

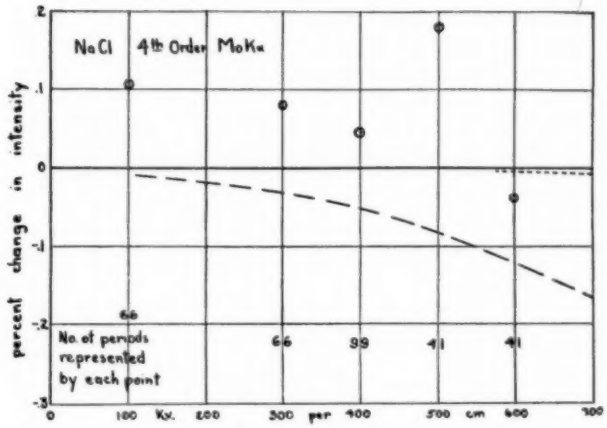

Fig. 3.

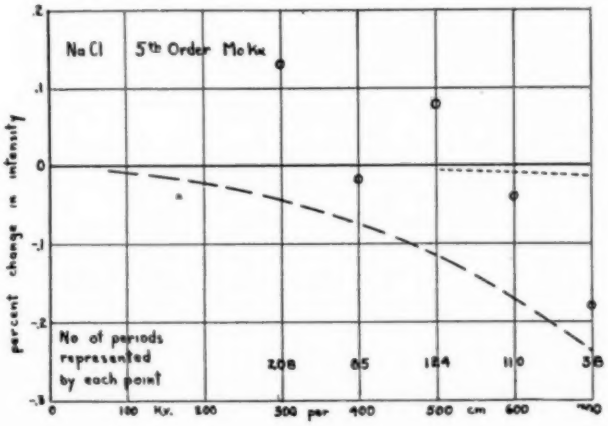

Fig. 4.

ber of periods averaged. Each period was 44.4 seconds, and approximately the first third of each interval was omitted to allow for adjustment of the recording system to a new value of ionization current.

Observations were made in the 4th and 5th order for rock salt and the 5th order for sylvine, the gradients ranging up to 700 k.v./cm. The tests under different gradients were grouped together in 100 k.v./cm. ranges, and the results are plotted in Figs. 3, 4 and 5.

The sensitivity of the apparatus was such that 1/30 of one percent in the 5th order could just be detected if the deflection were steady. However to reduce the fluctuations to this level it would be necessary to increase the

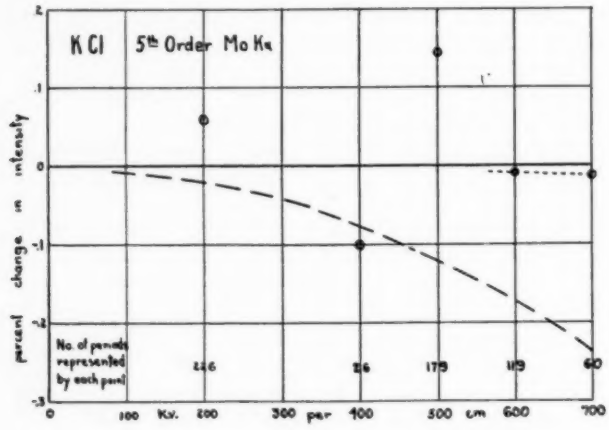

Fig. 5.

ionization current by a factor of $[1/(1/30)]^2 = 900$ which would hardly be possible. Increasing the electrostatic capacity of the recording system would be of no avail because there were irregular line voltage variations of about 1 percent.

Conclusions

The experimental results are not precise enough to tell definitely whether Hengstenberg's theory, the theory outlined above, or neither describes the effect. The 700 k.v./cm point on the 5th order NaCl curve falls very nearly at the value predicted by Hengstenberg's theory. It is doubtful whether this is more than a coincidence since it depends on a small number of observations. No other crystal stood this high field though many attempts were made to find one. The writer believes that from consideration of all the data, the effect is probably not as large as predicted by the Hengstenberg theory.

The KCl crystals used were very kindly furnished by Dr. E. F. Barker of the University of Michigan. I am also indebted to Professor A. H. Compton for advice and interest in this problem. The work was supported by the Utilities Research Commission as a part of their program of investigation of the properties of solid dielectrics at Ryerson Laboratory of the University of Chicago.

INFRARED FILTERS OF CONTROLLABLE TRANSMISSION

By A. H. Pfund
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(Received May 26, 1930)

Abstract

When using an echelette grating for work in the infrared it is necessary to eliminate overlapping, higher orders. Since no adequate series of true filters covering the entire infrared is known, a new type of filter has been developed. Essentially, this type of filter consists of a powder spread uniformly over a surface of polished speculum. Short wave-length radiations are reflected diffusely while long wave-length radiations are largely transmitted since the Rayleigh scattering for long waves is feeble. The region of transition from opacity to transparency is controlled by choosing powders of proper particle-size and by depositing these in layers of appropriate thickness.

Specific examples, involving the use of particles whose mean diameter covers the range: 0.22μ to 2.5μ, are presented to show how filters for almost any portion of the spectral range: 2μ to 7.5μ may be largely freed from the effects of superposed, higher orders. Filters for greater wave-lengths may be produced by much the same methods.

FOR the attainment of large dispersion and high resolving-power in the infrared, the diffraction grating, in particular, the echelette grating is coming into wide use. It suffers, however, from one drawback, i.e. superposed orders. If for example, an echelette grating be adjusted for work in the first order near 3μ, there is superposed on this a large amount of second order 1.5μ energy, third order 1μ energy, etc. Due to the fact that the usual Nernst lamp has its energy maximum near 1.6μ, the energy of the contaminating radiations exceeds greatly the energy at 3μ. It is proposed to discuss in the following a new type of filter which, though by no means perfect, does minimize the effect of contaminating radiations.

The term filter is here employed in the broad sense of being a device which either isolates narrow spectral regions or which experiences a change from opacity to transparency within a relatively small wave-length interval. To be specific, a satisfactory filter for an echelette grating, operating between the limits 3μ to 3.5μ, would be one which is quite opaque for all radiations shorter than 1.75μ and quite transparent for radiations greater than 3μ. To realize so great a change in transparency within so narrow a spectral range is difficult.

Methods now in use for filtering out the undesirable radiations are here enumerated: I. Infrared monochromator.[1] II. Residual rays.[2] III. Reflection from rough surfaces.[3] IV. True absorption filters.[4] Without going

[1] Sleator, Astro. Phys. J. **48**, 127 (1918).

[2] Rubens and Aschkinass, Ver. deutsch phys. Ges. **17**, 42 (1898).

[3] Gorton, Phys. Rev. **7**, 66 (1916).

[4] Coblentz, Supplementary Investigations of Infrared Spectra 5–7, Carnegie Inst. of Washington (1908).

A very comprehensive list of references, dealing with the infrared, is to be found in "Le Spectre Infrarouge" by Jean Lecomte, Les Presses Universitaires de France (1928).

into a detailed discussion of the various devices it may be stated that most of them are limited in the range of spectrum which can be covered; again, some lack flexibility, i.e. if true filters or crystals (employed for residual rays) fail to show high transmission or reflection, respectively, in the region to be studied, there is nothing to be done about it. As for reflection from rough surfaces it may be said that the wave-length interval separating regions of low and high reflection is entirely too great to be considered seriously for the present purpose.

The new filters about to be described are a by-product of some work that is being carried out on the measurement of particle-size of finely divided powders by studying their transmission in the infrared. Rayleigh's inverse fourth power law of scattering is strictly applicable only if the particle-size be small in comparison with the wave-lengths employed. If, however, the particle-size be large in comparison with the wave-length, the particles assume the role of small mirrors which reflect vigorously. Consequently, if transparent particles of a uniform and suitable size be produced it will be found that they reflect the regions of short wave-lengths strongly and scatter those of great wave-length feebly. Used in transmitted light a film of such small particles will be virtually opaque to the short wave-lengths and highly transparent to the longer. Body-color, involving true absorption, plays no necessary part in the functioning of these filters.

The pulverized materials used in the construction of such filters must fulfill certain necessary conditions: 1. The material must be highly transparent in the spectral region to be studied. 2. A large range of particle-sizes must be available, and the particles in any individual class must be essentially constant in size. 3. The substratum on which the pulverized film is deposited must be transparent. 4. The films must be of uniform thickness.

Concerning condition (1) it may be said that short of 20μ, oxides, sulphides and halides have been found most transparent. Thusfar the most satisfactory films have been formed by the process of "fuming" as, for example, by allowing the oxide fumes from burning magnesium ribbon to collect on a plate. Condition (2) is not as yet realized. It is to be pointed out, however, that methods for accomplishing this purpose are known. The well-known process of "air-flotation" and subsequent settling has been used. Again, the method of successive centrifugings has been employed for bringing about uniformity of particle-size. The nature of the substratum (condition 3) depends largely upon the spectral region to be studied. Microscope cover glass 0.2 mm thick will serve up to 4μ while a thin plate of rock-salt will be useful at least up to 18μ. In order to eliminate completely the element of transparency of the substratum the procedure of coating a polished speculum plate with the pulverized film has been adopted—particularly for the region of long waves. Such a mirror will reflect all wave-lengths while the film will reflect the short waves diffusely but will transmit the long ones regularly. Attention is to be drawn to the fact that, while the widest possible spectral range may be covered by using a speculum or some other reflecting surface, the performance of such a "reflection" filter is less satisfactory than that of

a transmission filter. The reason is that the diffusely reflected light of shorter λ is in part added to the regularly reflected light in the case of the reflection filter, but not so in the transmission filter.

A few examples of the performance of these filters are here presented. Measurements were carried out by means of a rock-salt spectrometer and thermopile. Since it is difficult to control the film thickness accurately, it is necessary to resort to the use of a spectrometer in order to decide when a film of the proper characteristics has been deposited. In Fig. 1 are presented "transmission" curves (*A* and *B*) for zinc-oxide which was fumed on microscope cover glass. The fumes were supplied by an arc burning between zinc

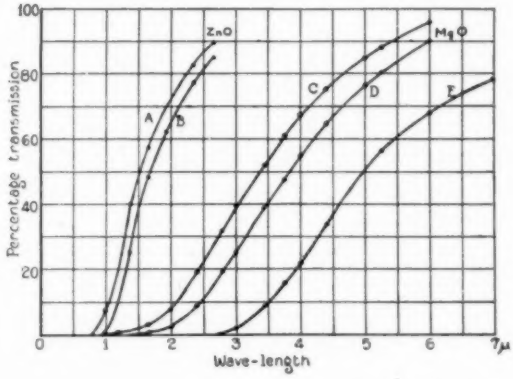

Fig. 1. Transmission curves for films of ZnO and MgO.

terminals. For the thicker film a deep, ruby-red image of an incandescant lamp filament was visible in transmitted light. A similar series for MgO, fumed on speculum is shown in curves *C*, *D* and *E* which apply to films of increasing thickness. In order to obtain the "incident energy" the oxide film was wiped off the speculum mirror.

It is known that zinc oxide particles are smaller than those of magnesium oxide. This is borne out by the curves which show that the transition region for ZnO lies at the shorter wave-lengths. While it is possible to shift this transition region somewhat in the direction of increasing wave-lengths by increasing the film-thickness, a limit is set to this mode of procedure as is evident from the decreasing slope of curve *E*, Fig. 1, in the region of high transparency. It is thus shown that, to produce filters for increasing wave-lengths, particles of increasing size must be used.

Even though a filter, as judged by its transmission curve, may appear to be entirely satisfactory, it is not necessarily so. The total energy associated with any wave-length is given by the product of the following quantities: 1. energy emitted by source. 2. transmission of total air-path. 3. reflection factor for the echelette grating, and 4. transmission factor for filter. This is illustrated in the following curves for films of increasing thickness. In Fig. 2 are plotted the true transmission coefficients of MgO plus cover glass while in Fig. 3 the actual energies are plotted for the same filters. The Nernst

lamp was operated at such a temperature as to place the wave-length of maximum emission at 1.9μ, no correction for irrationality of dispersion having been applied. It is this powerful maximum which must be rendered innocuous if regions of greater wave-length are to be studied. It is usually possible to realize any desired freedom from contamination from shorter wave-lengths; but this is accomplished at the expense of transmission. For the time being two arbitrary criteria for acceptable filters have been laid down, i.e. (1) the transmission, in the region under consideration, λ, must be at least 50%, (2) the energy at $\lambda/2$ ought not to exceed 5–10% of the energy at λ. Applying these criteria to specific filters it is evident that filter III, (Figs. 2 and 3) is

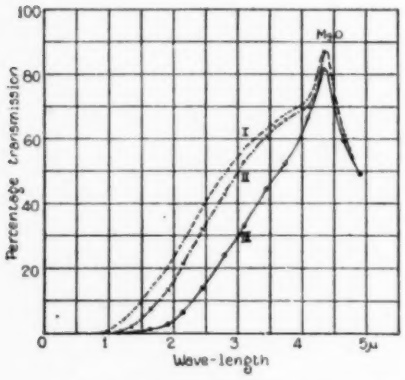

Fig. 2. Transmission curves for various thicknesses of MgO on glass of 0.2 mm thickness. Transmission of glass included in curves.

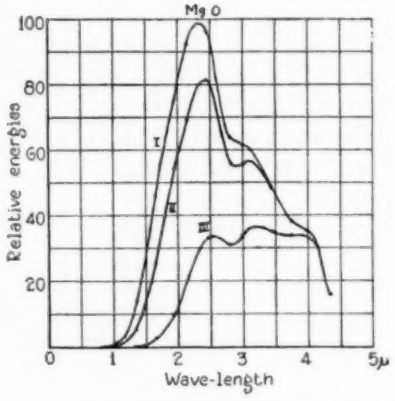

Fig. 3. Relative energies from Nernst lamp transmitted by same films shown in Fig. 2.

most satisfactory in the 3.75μ region. If a wedge-shaped film of oxide be deposited on an over-size speculum mirror, it is easy to pick out the position of the film having the best thickness. If, on the other hand, the film be deposited on microscope cover-glass the latter may be rotated about a vertical axis, thus changing the effective thickness of film, or again, a wedge-shaped film may be deposited.

While the deposition of fumed films is comparatively simple, it becomes difficult to make the thickness uniform whenever the pulverized material is furnished as a dry powder. It is proposed to form films of these materials by the well-known method of "air-flotation." For the time being, films were prepared by dispersing these pigments in water. A small amount of pigment and water were placed on a flat plate of glass and the mixture was ground to a paste of uniform consistency by means of a glass "muller." The latter was then used for applying the paste to the speculum surface. Unfortunately, films produced in this manner are non-uniform in thickness and, as a result the transition range is broadened out. While a graded series of NaCl powders would have been desirable it was found necessary to use such coarser particles as were available, despite the fact that they were known to have bands of

absorption in the region of longer waves. The series of filters shown in Fig. 4 were obtained through the use of the following powders whose respective average diameter of particle[5] is given in Table I.

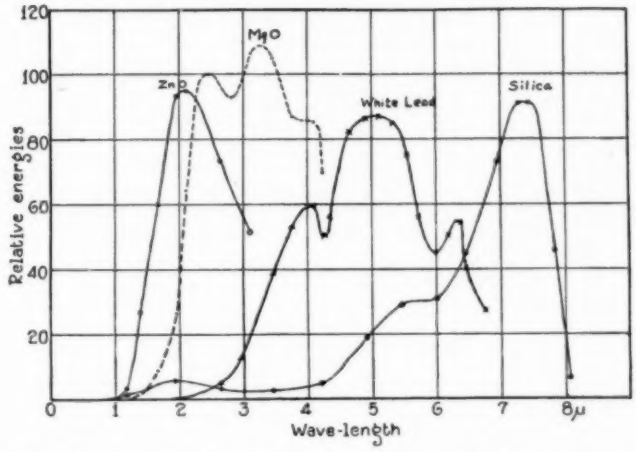

Fig. 4. Relative energies from Nernst lamp transmitted by various filters.

TABLE I.

Powder	Average particle diameter	Mode of application
I. Zinc oxide	0.22μ	Fumed
II. Magnesium Oxide	0.35	"
III. Basic carbonate of white lead	0.50	Water Paste
IV. Silica	2.5	"

These curves for relative energies are so plotted that the maxima have approximately the same heights. Inspection shows that a very fair degree of separation between short and long waves has been effected and that, each filter may be used to advantage in the region of maximum energy. In fact it is evident that, following this general mode of procedure, a filter for almost any desired spectral region may be produced.

The sharp drop of the curve for Silica (SiO_2) near 8μ is due to the true absorption of this material; the same may be said for the sharp drop at 7μ for basic carbonate white lead. In this connection it may be stated that the writer has on record a large number of "transmission" curves for films of powdered sulphates and carbonates spread on polished speculum. These curves reveal a great deal more complexity than do the curves obtained by reflection from polished crystals. The results will be published at a later date.

In carrying out precise measurements with an echelette grating, together with these new filters, it is essential that the slight effect of superposed orders, higher than the first, be taken into account. To accomplish this, it is neces-

[5] The measurements of particle-size were kindly carried out by Mr. G. S. Haslam of the Research Laboratory of the New Jersey Zinc Co.

sary to procure a series of filters whose characteristics are exactly the reverse of those already described. To be specific, if the 4μ region be studied, it is necessary to procure a filter which is entirely opaque at 4μ and highly transparent at 2μ and at all shorter wave-lengths. Fortunately, this problem is relatively simple. As is well known, layers of water, glass, quartz, fluorite, etc., when given the proper thickness, can be made to fulfill the conditions imposed on this type of filter. In this connection it is to be stated that, if nonaqueous filters be desired in the region of the near infrared, corex glass and a urea-formaldehyde condensation product known as Pollapos, are very effective. Corex glass of 3.2 mm thickness is opaque at 3μ while Pollapos of 4.5 mm thickness transmits virtually nothing at 1.6μ. It is hardly necessary to add that the effectiveness of a powder-filter can be increased by choosing a light source such that the emission of shorter wave-lengths is suppressed while that of the longer ones is enhanced as, for example, in case of the Welsbach mantle.

This report is incomplete since specific direction for powder filters covering the entire range of the infrared are not available. It is felt, however, that having described the general mode of procedure, the individual investigator will be guided in the production of filters required for his special needs.

VELOCITY OF ULTRASONIC WAVES IN WATER VAPOR

By George E. Thompson
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(Received May 22, 1930)

Abstract

The velocity of sound waves having a frequency of 108,600 cycles per second, has been measured in water vapor by a method similar to that used by Pierce for other gases. At a temperature of 27° C. the velocity is 432 meters per second.

SOME results by Pierce[1] for the velocity of ultrasonic waves in air showed much less than the expected variation of velocity with change of humidity. This situation suggested the desirability of making similar measurements in pure water vapor, so the present work was undertaken. More recently Reid[2] found the effect due to humidity which was expected on the basis of theory. It still seemed worth while, however, to continue the work with water vapor along the line originally planned.

Description of Apparatus

The sound chamber consisted of a cylindrical brass tube of 9.5 cm inside diameter and 25 cm in length. A plane reflector about 9 cm in diameter was moved back and forth by the calibrated screw *S*. (See Fig. 1) In order to

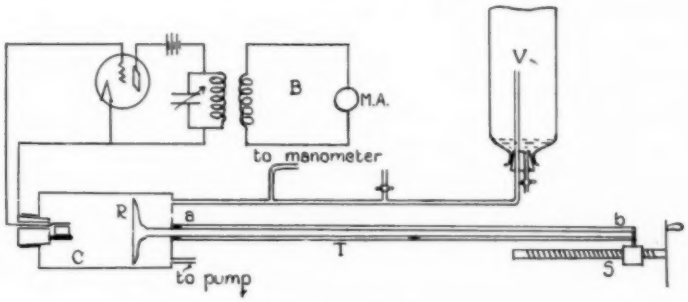

Fig. 1. Diagram of apparatus.

get an air tight joint at *a*, the rod carrying the reflector was enclosed in a rubber tube which was fastened to the sound chamber at *a* and to the rod at *b*. This arrangement permitted the reflector to be moved back and forth easily, the rubber being stretched or contracted to accomodate the motion of the rod. The rod was about 150 cm long. A spiral spring was placed around the rod and inside the rubber tube to keep the tube from gripping the rod when the pressure was reduced inside the chamber.

[1] G. W. Pierce, Proc. Am. Acad. of Arts and Sciences **60**, No. 5 (1925).
[2] C. D. Reid, Phys. Rev. **35**, 814 (1930).

The quartz crystal was mounted between electrodes on the end of a brass plug which was carefully ground to fit a tapered opening at the end of the chamber. The wire leading to the upper electrode of this crystal holder was insulated by filling the hole through which it passed with sealing wax. The lower electrode was not insulated from the plug so that connection to it was made by soldering a wire to the outside end of the plug.

The vapor was generated in a glass bottle *V* and pumped slowly through the chamber *C* during the course of the experiment. It was necessary to keep the pumps working continuously because the apparatus was not quite vacuum tight, the leak with the pump idle amounting to about one half centimeter of mercury pressure per hour.

The electrical circuit is fully shown in the figure and needs no detailed description. Instead of making observations on a d.c. meter placed in the plate circuit of the oscillator tube, a Weston, model 412, high frequency milliameter (2 m.a. range) was placed in a resonant circuit which was coupled loosely with the oscillator. This circuit had a resistance of over 700 ohms and consequently tuned very broadly.

The temperature of the vapor was measured with a copper-constantan thermocouple placed in front of the crystal but above the direct path of the sound waves.

Method of the Experiment

Absolute measurement of velocity was not attempted. The velocity of the waves in air was assumed to be known and the velocity in the vapor determined by comparing the wave-length in vapor with the wave-length in air. In water vapor the crystal oscillations were somewhat irregular so that high precision of measurement could not be attained easily. Also the milliameter fluctuations caused by the motion of the reflector were very slight due to the low density of the vapor. This difficulty was partly overcome by using a microscope to observe the movement of the pointer of the meter. In making measurements, the reflector was placed about 2.5 cm from the crystal face and at a position of minimum deflection, and the position read on the screw. Another position 20 half wave-lengths farther from the crystal was found and another reading taken. The settings were always made with the screw turning in the same direction.

Source of Error

It was considered likely that the greatest source of error would be the lack of purity of the vapor caused by air leakage. Consequently, extremely accurate measurement of temperature, pressure, frequency, and wave-length were not attempted.

In order that the wave-length be proportional to velocity the frequency of the crystal must not change when the nature of the surrounding gas is changed. A second oscillator was heterodyned with the crystal oscillator to give a beat note of about 200 cycles per second. Since no very appreciable change of pitch was produced by changing from air to water vapor, the frequency control was deemed satisfactory.

The screw was calibrated by comparison with a Gaertner comparator and found to be of sufficiently uniform pitch, the maximum variation from the average being about 0.009 mm. The average pitch was 2.509 mm.

RESULTS

The wave-length in air at 22°C was found to be 3.176 mm. Considering the velocity to be 345 meters per second, the frequency figures out to be about 108,600 cycles per second.

In Table I are values for the wave-length in water vapor. These are given in terms of the pitch of the screw and changed to mm after averaging.

TABLE I. *Wave-lengths in water vapor.* (Average, $1.586 \times 2.509 = 3.979$ mm, Vapor pressure, 1.4 cm of mercury, Temperature, 27°C).

1.581	1.585	1.566	1.597
1.610	1.605	1.591	1.600
1.593	1.567	1.588	1.588
1.576	1.572	1.597	1.572
1.575	1.576	1.604	1.572
1.588	1.596	1.578	

With the data of Table I, we get for the velocity of sound in water vapor at 27°C.

$$V = (3.979/3.176) \times 345 = 432 \text{ meters per second.}$$

Masson gives 401 meters per second as the velocity in water vapor at 0°C. Although no factor for temperature correction is available it seems that Masson's value is considerably below the value given above. Failure to provide air-free vapor for the determination would account for the low value. Since the effect of air in the vapor is to decrease the velocity, the largest value one can obtain for the velocity would presumably be most reliable.

With the value for the ratio of specific heats and density of water vapor given by Neyreneuf[3] we get a theoretical value for the velocity of sound in water vapor at 27°C which is $V = 348(1.321/0.6143 \times 1.402)^{\frac{1}{2}} = 431$ meters per second. Neyreneuf's data were given for saturated vapor, whereas, the vapor pressure used in the present experiments was only slightly more than half that of saturated vapor. On the whole, the agreement is quite satisfactory, considering the errors involved in the measurement of the various quantities.

[3] Neyreneuf, Annals de chimie et de Physique **9**, 535, (1886).

UNRELIABILITY OF PHOTOGRAPHIC EMULSIONS ON GLASS FOR RECORDING DISTANCES AND A METHOD OF MINIMIZING THIS DEFECT

By D. Cooksey and C. D. Cooksey
Sloane Physics Laboratory, Yale University

(Received May 19, 1930)

Abstract

Superficial motions of double coated emulsions were investigated by Schlesinger's ink dot method. Also the positions of developed images with respect to corresponding latent images were studied for singly coated plates. Apparently *there are stresses in undeveloped gelatin emulsions that can be relieved* before plates are used for photographic purposes by soaking them in water followed by dehydration in alcohol, *thus greatly enhancing their reliability for recording distances.* This process we have termed *normalizing.* The maximum observed change in a distance between images, in their latent and developed states on a singly coated plate was 9μ without normalizing and 2.2μ with normalizing. The average change was likewise reduced to about one quarter. The advantage of normalizing is emphasized by the results reported in another paper.

MUCH effort has been expended in determining what reliance may be placed on photographic emulsions when used for recording the relative positions of star images and spectral lines. Many things affect the answer to this question. A very complete account of this subject, with bibliography, has been given by F. E. Ross.[1] Some years ago Professor Frank Schlesinger,[2] and recently E. Bäcklin,[3] reached the conclusion that the position of a latent image is not appreciably altered in the processes of development. Schlesinger used a method of investigation in which artificial star images were produced on a photographic plate by spattering it with water-proof india ink. This plate was subjected to the ordinary developing, fixing and washing processes, except that the developing agent was omitted from the developer. The coördinates of a large number of ink dots were accurately determined before and after development. He reached the conclusion that any error due to distortion of the gelatin was negligible in comparison with the errors of measurement, and has since informed us that a subsequent unpublished investigation has led to the same conclusion.

During our work on the development of the "method of displacement" for measuring x-ray glancing-angles, we built and tested a specially designed spectrometer.[4] The mechanical errors in this instrument and also the errors of manipulation were so small that they were negligible compared to the errors of measurement of distances between spectral images on photographic

[1] F. E. Ross, "The Physics of the Developed Photographic Image." Van Nostrand (1924).
[2] F. Schlesinger, Publications of the Allegheny Observatory, Vol. I, No. I.
[3] E. Bäcklin, Inaugural Dissertation, Upsala (1928).
[4] C. D. Cooksey and D. Cooksey, following paper. This issue.

plates. As this method is based partly on the assumption that the emulsion surfaces are plane and parallel, we decided to obtain plates more suitable for this purpose than those sold commercially. Through the kindness of Dr. C. E. K. Mees, the Research Laboratories of the Eastman Kodak Co. furnished us with "parallel plate" glass coated with a double thickness of x-ray emulsion. Several spectrograms of the $K\alpha_1$ line of silver were taken on these plates. Corresponding distances between images, which should have been constant to less than one micron, were found to differ between plates by as much as ten microns, a difference altogether too large to be accounted for by instrumental errors or those of measurement. In consequence, we were forced to suspect the constancy with which the position of a latent image is retained by its developed image, at least in the case of these double coated plates.

To investigate this, we adopted a modification of Professor Schlesinger's method. Plates were cut in strips 25 cm long and 3.4 cm wide (the size used for spectrograms) and spattered with water-proof india ink along their longer center-lines. The distances between ink dots were measured on a carefully calibrated Gaertner measuring engine, which is fully discussed in another paper.[4] The errors of the screw, bearings and divided head were eliminated by always using exactly the same portion of the screw for the remeasurement of a given distance. The screw coördinate of each edge of each selected ink dot was determined three times. From the mean of these three determinations the distance between dot centers was obtained. The plates were measured before and after they were subjected to various soakings, dryings and development. The so-called developer used contained sodium sulphite, sodium carbonate and potassium bromide in the usual proportions, but no developing agent. The fixing bath contained sodium thiosulphate, sodium sulphite and acetic acid, but no alum or other hardener.

Preliminary investigations showed, as others had previously found, that the reliability of the gelatin was very dependent on the method of drying after development and washing. The essential factor in drying is that it shall take place uniformly. This condition is approached when the water is displaced from the gelatin by immersing the plate in strong ethyl alcohol; but as the alcohol will displace more water than is normally contained in the gelatin, the plate, if exposed to dry air, will become cloudy as the alcohol evaporates. This may be completely overcome by evaporating the alcohol in a humid atmosphere such as that in a box lined with wet blotting paper. As this part of the work was done in the summer, when the humidity is high, it was unnecessary to take this precaution. Furthermore we were led to believe that there were superficial longitudinal stresses in this gelatin, introduced while the emulsion was cooling during the process of manufacture. In order to relieve these stresses, plates were soaked in water for thirty minutes, dried in alcohol for twenty minutes and finally left to attain equilibrium in a humid atmosphere. This process, as applied to fresh plates, we have termed *normalizing*.

The accuracy of the measurements can be estimated from the following

data. The average variation of one setting from the mean of three settings on a given dot edge, obtained from 282 settings on 39 ink dots, was 0.19μ before, and 0.14μ after development, with a maximum variation from the mean of 0.7μ and 0.6μ respectively. The difference in accuracy is due to the difference in illumination before and after the silver salts had been removed. Eighteen distances on a developed plate, varying from 0.01 to 60 mm in length, were remeasured according to the above procedure on three different days during the course of a week. The average of the differences of these three determinations from their means was 0.09μ with a maximum variation of 0.3μ. Table I gives changes observed in distances between ink dots on a series of seven plates, measured before and after the plates were subjected to the treatments specified.

TABLE I. *Comparison of changes in distance between ink dots on double coated plates resulting from various treatments.*

Treatment before measurement	remeasurement	No. of distances	Maximum change, μ	Average change, μ
None	developed and dried without alcohol	3	3.7	2.5
None	any wetting process and dried with alcohol	3	4.1	1.8
Wetted and dried with alcohol	wetted and dried with alcohol again	45	0.8	0.32
None	normalized	22	4.9	1.35
Normalized	developed and dried with alcohol	36	0.8	0.3

(By "developed" is meant 5 minutes and 20 minutes respectively in the developer and fixing bath described above, and 30 minutes in running water.)

These results seem to indicate that normalizing relieved stresses, thereby reducing the average relative displacements on development to about one-fifth. They lead to no conclusions as to the motions that may occur at the glass-gelatin surface or in intermediate layers. In connection with these results, Dr. Mees pointed out that certain precautions used in the manufacture of commercial plates were omitted by the Research Laboratory in preparing these double coated plates for our use.

In order to determine the reliability of the position of a developed image with respect to that of its latent image, the work was continued as follows. We constructed a template, about 78 mm long and 17 mm thick, of steel with ends lapped plane and parallel. Two parallel slits at a fixed distance apart were formed by bolting similarly prepared blocks to the ends of the template, the width of opening of the slits being adjusted to less than 0.02 mm by shims. By allowing x-rays to pass through the slits onto a photographic plate clamped to the template, very sharp-edged lines were obtained. Thirteen strips 3.4 cm wide were cut parallel to the 5 inch side of four 5×7 Eastman Universal plates taken from the same box. The emulsion of these plates is about 0.025 mm thick. The template, or rather the slits which terminated it, was photographed with x-rays approximately centered on ten of these strips. All thirteen strips were then normalized and the template rephoto-

graphed on nine of the strips, including, of course, some of those already bearing latent images. The strips were finally all developed in "Eastman X-ray Developer," fixed and washed. After washing they were soaked in strong alcohol for about 10 minutes and then dried in a humid atmosphere. The results of the measurements on the developed images are given in Table II.

TABLE II. *Comparison of reliability of normalized and unnormalized singly coated plates.*

	Unnormalized	Normalized
Number of distances measured	10	9
Maximum difference in lengths measured	9.0μ	2.2μ
Average difference from the mean	2.8μ	0.7μ
Probable error of one determination	$\pm$2.2μ	$\pm$0.5μ

As all these plates were handled in the same manner and subject to the same uncertainties of measurement, it is obvious that the *reliability of a photographic plate as a recorder of definite distances is greatly enhanced by the normalizing process.* However, by taking proper precautions during the process of manufacture, it might be possible to avoid the introduction of these stresses here relieved by normalizing. The fact that local stresses, due to non-homogeneity or other causes, may exist in gelatin, and do cause shifts of images by as much as 2μ is thoroughly treated by Ross. However, he states that 2μ is the maximum shift to be expected. We wish to call particular attention to the fact that we have found occasional motions as large as 9μ which occurred due to the relief of stresses existing in singly-coated commercial plates, and that if such stresses are not relieved before such a plate is used, it will not be reliable for positional recording. It would therefore seem to us advisable to subject plates to a normalizing process when they are intended for use in recording unique occurrences, such as eclipses, if intervals between images are of prime importance. Even when images may be recorded on many plates, given that the resulting definition permits of measurement to less than 2μ, normalizing will increase the self-consistency of measurements between plates in proportion to the accuracy of the individual measurements, as long as other causes of variation do not enter, such as pressure shifts of spectral lines, etc. This statement is, we hope, clearly verified by Table XI of another paper.[4] It might not be amiss here to emphasize a point clearly demonstrated by Ross (page 197)[1] but contrary to what has been commonly assumed as an excuse for variations of measurements; viz., the non-uniformity of image contours. Our experience, in common with Ross's, is that well filled, sharply outlined images are just as liable to a shift as their "moth-eaten" relatives.

The particular object of this investigation was to determine a reliable method of handling spectrograms of sensibly the same dimensions as used by us in determining glancing-angles. During the course of the work we made certain observations which we did not feel called upon to verify because the normalizing process and subsequent drying with alcohol proved satisfactory for our purpose. However, we shall suggest conclusions which may be drawn

from them in the hope that they may be of interest. The edge-effects referred to by Ross and others have been reproduced by us, both with ink dots and developed images. The motions referred to in our tables are not due to edge effects, but frequently occur in the central region of the strips within a length of two or three millimeters. We found that we could control at will the direction of motion of an image by removing a strip of gelatin parallel to the image and at a distance of one centimeter or less from it. The evidence thus obtained, although not conclusive, indicated a compound effect made up of two independent causes; one, the diffusion of silver grains away from the drying edge* ("hydration gradient," cf. Ross), and the other, a contraction of the gelatin causing a bodily shift of the matrix toward the dried edge. It is believed that the former of these causes might readily change the scale of a photograph, in the region drying last, when alcohol is not used for dehydration.

We have been informed that gelatin, with or without the silver halides, normally contains about 15% water. One attempt was made to do away with the necessity of evaporating in a humid atmosphere by using about 75% alcohol. The resulting plate was free from clouding, but large stresses persisted in the gelatin. We therefore were content with the successful technique which employed the use of ethyl alcohol, at least 90% pure, and evaporation in a humid atmosphere. As the surface tension of alcohol is low, dirt specks adhere to the gelatin. Consequently all dust particles should be removed before the plate is placed in the alcohol, which in turn must be dust free. Although the plates used were soaked face up, we would suggest immersing them horizontally face down. If a plate is immersed standing in an approximately vertical plane, the gelatin will dry with ridges across its surface as though the displaced water had flowed down in tiny rivulets. The alcohol was evaporated with the plates in a plane making 45° with the horizontal, gelatin side up, and resting diagonally on one corner. However, we found no evidence to show that the drying position made any difference on alcohol soaked plates.

In conclusion we wish to express our indebtedness to Professor Frank Schlesinger and to the late Professor B. B. Boltwood for helpful suggestions in connection with this investigation. We are also indebted to Professors McKeehan and Uhler for advice in connection with the presentation of this work.

* Dr. Mees informed us that silver grains would diffuse into the region more highly saturated with water.

PRECISION MEASUREMENTS OF THE GLANCING-ANGLE OF REFLECTION FROM CALCITE FOR SILVER ($K\alpha_1$) X-RAYS BY THE "METHOD OF DISPLACEMENT."[1]

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Abstract

Part I. Method of displacement.—This method permits the determination of glancing-angles in terms of *linear measurements only*. It consists in letting a properly limited beam of x-rays, after reflection, fall on a photographic plate placed successively in two parallel positions which differ in distance from the crystal by a known amount. The theory of the method and its practical application to the present case are briefly discussed with references to Uhler's paper.

Part II. Apparatus and Adjustments.—A new high precision spectrometer, including a specially designed bearing on which the crystal rotates and a unique form of plate holder using air pressure to ensure the flatness of the photographic plate, is fully described. A *special* form of hot filament *cathode* which gives an approximately *linear source* of x-rays has been originated. Precision methods for adjusting and testing the reliability of the instrument are discussed at length. It is believed that the instrument is free from any defects that might cause a constant error of as much as 0.04″ in the glancing-angle.

Part III. Experimental prodedure.—The cleavage planes of a nearly perfect specimen of Iceland spar were used as grating. The bearing of its perfection on the widths of the spectral images is discussed. *The coefficient of expansion of calcite* normal to the cleavage planes was computed from the most reliable data obtainable. A mean value which is sufficiently precise, over a sixteen degree range, to reduce values of glancing-angles to 18°C within 0.008″ is $1.02_3(10)^{-5}$ per °C. Attention is called to the fact that the commonly used value $1.04(10)^{-5}$ is not a sufficient approximation.

Distances between spectral images on each negative were measured on a Gaertner measuring engine, the errors of which were carefully investigated. The "displacements" of the photographic plate were equal to fixed intervals marked on a measuring bar and calibrated against the screw of the same measuring engine. The accuracy of these measurements and the effect of their errors on the glancing-angle are discussed.

The experimental procedure and precautions used in taking and measuring spectrograms are fully described. A complete protocol of observations is given for one plate. Evidence for the accuracy of the measurements is presented and discussed.

Part IV. Results.—The weighted mean value of the glancing-angle for the $K\alpha_1$-line of silver from the cleavage planes of calcite at 18°C is 5°17′ 13.81″ ± 0.06″ giving a wave-length, if $\log 2d_{18} = 0.7823350$, of 0.558238A. This result is compared with those of other observers. It differs from Kellström's value quoted by the Int. Crit. Tables by more than ten times the combined probable errors. The only probable source of an adequate constant error in either result seems to lie in the crystal. Compton's measurements of the density of calcite are invoked to prove that different specimens of Iceland spar do differ enough in density to account for more than the discrepancy, if changes in density and grating space are interdependent.

[1] The final numerical results published in this paper have already been given by us in a letter to the Phys. Rev. [2] **35**, 564 (1930) and Nature **125**, 461 (1930).

Part I. Theory of the Method of Displacement

VERY precise methods have been developed for measuring the glancing-angles at which characteristic x-rays are reflected by a crystal. In most cases where the highest precision has been attained, the results are based on measurements with a divided circle. In 1917 H. S. Uhler,[2] of this laboratory, suggested the so-called "Method of Displacement," by which glancing-angles are computed from linear measurements only. The method was given a preliminary trial, at the time, by Uhler and one of us[3] and gave results of greater accuracy than any hitherto reported. The present work was undertaken for the purpose of developing this method to the high degree of precision of which it seemed capable. Unforeseen difficulties delayed the work until divided circle methods had been developed to give a precision that we could not expect to surpass. However, glancing-angles are of such importance that, it seemed to us, their values should be checked by an independent method of equal reliability, and therefore the work was continued.

The method is a photographic one and "consists in taking one exposure when the plate is at a certain distance from the crystal and then a second exposure when it is at a different distance from the reflector. The displacement of the spectral image, corresponding to some one wave-length, is a function of the distance through which the plate has been *translated* parallel to the collimation line. The form of the function and the details of the calculation of the glancing-angle depend respectively upon the value of the constant angle between the normal to the plate and the collimation line, and upon whether the measurements are absolute or are based upon adjacent images pertaining to known wave-lengths. The interval of translation may be determined with ease and great accuracy, whereas only an approximate value of the distance between the plate and the axis of rotation is required in any case."[2] It involves the fundamental assumption that the plate, in each of its chosen positions, intersects a region of the reflected beam in which the intensity is symmetrically distributed about a line which makes an angle with the axis of the incident beam equal to twice the glancing-angle. Such a region can be obtained approximately, in the case of a *perfectly selective* reflector, if the incident beam completely fills, and is limited by, two narrow slits whose long axes are parallel to the axis of rotation of the reflector; provided that the aperture of the beam in the plane of the long axes of the slits is sufficiently limited. The region then lies between the Bragg foci of the two slits. The condition that the reflector be *perfectly selective* is not fulfilled by real crystals, but it will be shown later that the crystal used in the present work reflected a beam of the required symmetry.

The function by which the glancing-angle can be computed from the measured data is easily derived from the geometry of Fig. 1. This figure is drawn in a plane which is perpendicular to the mutually parallel long axes of slits S_1 and S_2, axis of rotation and reflecting planes of the crystal. For simplicity the axis of rotation is assumed to intersect the line of centers of

[2] H. S. Uhler, Phys. Rev. [2] 11, 1 (1918).
[3] H. S. Uhler and C. D. Cooksey, Phys. Rev. [2] 10, 645 (1917).

the slits and to lie in the mean reflecting plane of the crystal, but the final result is independent of these assumptions. O is the point of intersection of the axis of rotation with the axis of the incident beam XX'. ORR' and OLL' represent reflected rays on either side of the direct beam and inclined to it at twice the Bragg angle of reflection, θ. LR and $L'R'$ are the parallel traces of the photographic plate in its two positions and intersecting the reflected rays at the points L, R and L', R' between the Bragg foci of the slits. The central ray, XX', intersects the plate at the points C and C' and makes the angle ω with the normal to the plate, OPP'. The dotted lines LL'' and RR'' are drawn parallel to XX'.

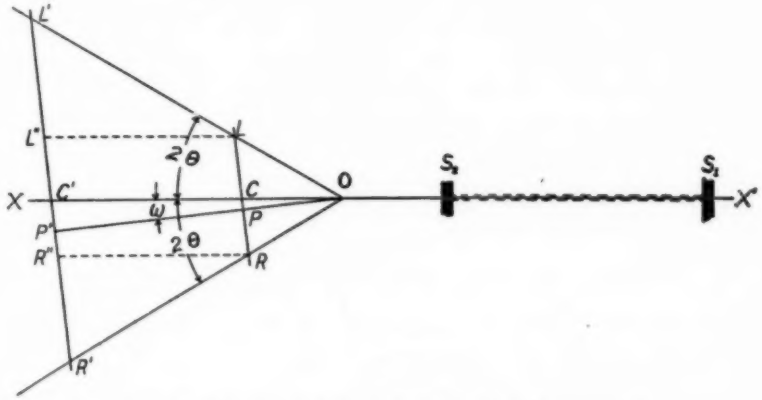

Fig. 1. Geometry of the "Method of Displacement."

If $x \equiv R'R''$, $y \equiv L'L''$, and $D \equiv CC'$, the angles θ and ω are given by

$$\tan 2\theta = \frac{2xy}{D(x+y)}\left[1 - \frac{D^2(y-x)^2}{4x^2y^2}\right]^{1/2} \tag{1}$$

$$\sin \omega = \frac{D(y-x)}{2xy} \tag{2}$$

If the plate is translated in the direction XX', the quantities x and y are respectively equal to the distances between corresponding spectral images on each side of the image of the direct beam, and D is the distance the plate has been displaced. But if the direction of translation is inclined to XX', the images of the undeviated beam taken in the two positions of the plate will not be superposed, and their separation must be measured and used in computing x and y from the separation of the spectral images. If is not difficult, in practice, to make this inclination so small that D may be taken as the distance the plate has been displaced in its line of motion without sensible error, but a corrected value of D can always be computed from this distance and the separation of the central images.

The quantity within the brackets in Eq. (1) is $\cos^2 \omega$, and therefore this term has very little effect on the value of θ, if ω is small. For small values of ω, the effect of this factor will be a maximum for glancing-angles in the

neighborhood of 22°.5. Even if ω is as great as 3.5′, the omission of $\cos^2 \omega$ only causes an error of 0.03″ at such glancing-angles, and at 5°, the region under investigation, the error is only 0.01″. When $\cos \omega$ and the central image displacement can both be neglected, the glancing-angle may be computed with sufficient accuracy from

$$\tan 2\theta = \frac{L'R' - LR}{2D}. \tag{3}$$

Thus the result depends on the measurement of intervals—LR and $L'R'$—each of which separates spectral images taken with the plate in a single position. This is an advantage if the spectral images corresponding to different positions of the plate have not the same width, and it is desired to use parallel hairs in the eye-piece of the measuring microscope.

A very full discussion of the geometry of image formation as applied to plane space-gratings, treated as perfectly selective reflectors, is to be found in Uhler's paper.[2] We therefore omit a detailed consideration of the effects of extreme rays and of inaccuracies in adjustment, and will merely cite these effects and the precautions taken to eliminate them in a later part of this paper.

Part II. Apparatus and Adjustments

The work was begun on an apparatus, designed by one of us,[4] but the results obtained lacked the accuracy of which the method was capable. Investigation showed the following defects: the apparatus as a whole was not sufficiently rigid; the plate-holder did not make the photographic plate flat and could not be displaced without fortuitous rotations; various parts of the apparatus were subject to distortion by small changes of temperature; and the axis about which the crystal rotated was indefinite. It was decided to build a new spectrometer which would be subject in use to no distortions causing a motion of one part relative to another of as much as 0.25μ. We are deeply indebted to Mr. Paul M. Mueller, then in charge of the Gauge Department of the Pratt and Whitney Machine Tool Co. of Hartford, Conn., for the design of a new spectrometer and plate-holder, which were built by that company under his constant supervision. The bearing for rotating the crystal was designed by him, and the unique form of plate-holder finally adopted was his original idea. We are also grateful to the Pratt and Whitney Co. for their very careful construction of the instrument.

Fig. 2 shows a view of the essential parts of the apparatus as set up for taking spectrograms. It is a tracing made from a photograph, and the wooden measuring stick, one-half meter long and divided in centimeters, fastened to base A, shows the scale in one direction. The radius of the divided circle table L is 13 cm, and the webbing of the castings varies in thickness from 1 to 1.5 cm. The whole assemblage weighs about 200 kg and rests on a stone-topped brick pier.

The primary base A is a standard Pratt and Whitney measuring engine bed, made of cast iron and aged by exposure to the weather for several years,

[4] C. D. Cooksey, Phys. Rev. [2] **16**, 305 (1920).

after having been machined. The maximum vertical depth of the casting is 25 cm. The upper surface is 146 cm long and consists of two parallel ways or rails separated by a T-slot. The farther way is flat; the nearer is, in cross-section, an inverted 90° "V", truncated. After strains had been relieved by aging, the ways were scraped straight to conform to a "master." This base is supported on three leveling screws, furnished with lock nuts, one of which is near the forward end and directly under the center line between the ways. The bracket M which carries the forward slit S_1 fits the track and, when in use, is locked directly over this foot.

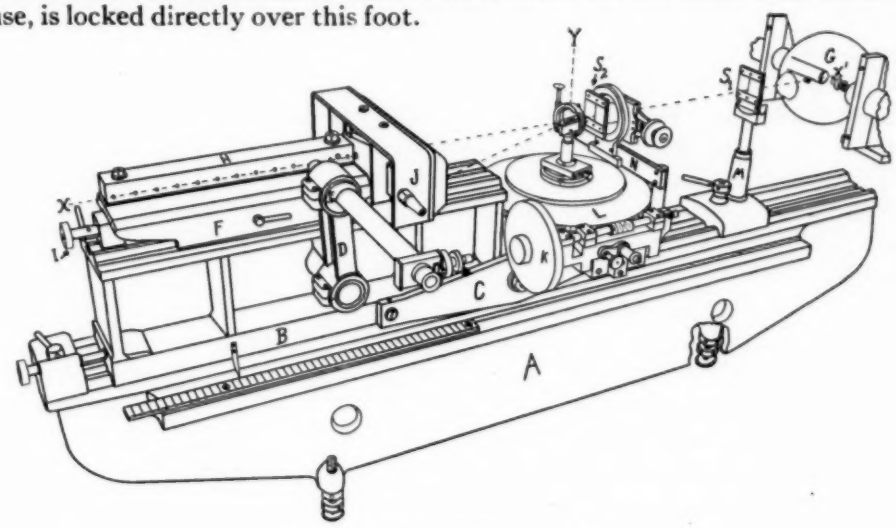

Fig. 2. Spectrometer assemblage.

The secondary base B is an iron casting in the form of an "I" beam, reenforced with heavy vertical cross webs. It is 56 cm long, 11.5 cm wide at top and bottom, and 16.5 cm high. The bottom surface was machined and scraped to fit the rails of base A accurately, so that B may be considered an integral part of A when locked in place. Thus, any bending stress due to a load on B will be resisted by a section of cast iron 41.5 cm deep. The position of B relative to A may be adjusted and fixed by means of the screw and clamp shown at the left of B. The upper surface of B consists of a track, a vertical cross-section of which is shown in Fig. 3.* The straightness and rigid-

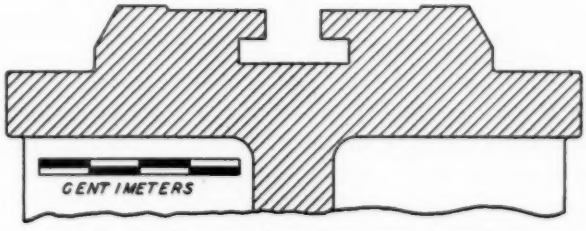

Fig. 3. Cross-section of ways on base B.

* Ways of this type were chosen because they have a vertical axis of symmetry and therefore permit the reversal of the "master" during the process of scraping the ways straight.

ity of these ways are essential to the success of the displacement method, as it is along them that the plate-holder carriage is moved. The scraping of the bearing surfaces of this track was done with extreme care. When assembled the track on *B* is very nearly parallel to that on *A*.

The plate-holder carriage *F* (the forward end of which is also shown in Fig. 4) rests on the track on *B*. It has bearing surfaces 15.5 cm long which were scraped to fit this track with great accuracy. It is provided with a slow motion adjusting screw *I*, and may be locked in position by a clamp operated by a level seen just to the right of the letter *F*. A portion of its upper surface was scraped flat and in the assemblage is parallel to the upper surfaces of the track on *B*, and serves as a seat for the measuring bar *H*. The forward end of the carriage is a vertical "goose-neck" having a horizontal hardened steel plate bolted to it. This plate has a "V" groove milled across its upper surface and serves as a support for the plate-holder *J*. The carriage with the bar and plate-holder weighs 15.1 kg.

H is a standard 12 in. Pratt and Whitney steel measuring bar, adapted for our use. The lower and back surfaces are scraped flat. In the front surface are thirteen hardened steel plugs with their outer ends ground and polished so that their surfaces lie all in one plane, parallel to the opposite surface of the bar. The plugs are numbered from left to right, beginning with zero and each has a very fine line, ruled with a diamond. The lines are accurately parallel and are approximately perpendicular to the lower surface of the bar. The distances between successive rulings are very accurately 1 "U. S. inch" each. The bar is held in place on the carriage by a tapered dowel pin which fits in a reamed hole at the left end of the bar. Two horizontal set screws (one of which is shown at *V* in Fig. 4) near the right hand end of the bar bear against a stud in the carriage which passes through an oversized hole in the bar. This permits the adjustment of the plane of the ruled plug surfaces parallel to the line of motion of the carriage.

The axis marked XX' in Figs. 1, 2, and 4 is defined as a line parallel to the line of motion of *F* and intersecting *Y*, the axis of rotation of the crystal, at the fixed elevation of the center of the slit S_2.

The microscope bracket *D* clamps to a short hollow cylinder which is bolted to a scraped surface on the central web of base B. The microscope is clamped in an eccentric collar *E* in the upper end of the bracket, and can be adjusted to any desired position. It is of 75-power and has a micrometer eye-piece. The movable reference lines ("crosshairs") are two fine diamond rulings on a glass plate and intersect at an angle of one radian. When the microscope is in proper adjustment the bisector of this angle is parallel to the vertical fiducial lines on the plugs of the measuring bar. An axial illuminator can be mounted on the forward end of the objective housing.

The bearing mechanism for rotating the crystal, and the slit S_2, are supported on a base which somewhat resembles a sled, the two runners of which embrace the lower edges of the base *B*. The nearer of these runners is shown in Fig. 2 and is labeled *C*. This base can rotate about an accurately fitting horizontal trunion bolt which passes transversely through the runners and *B*.

The lock nut and washers of the nearer end of this trunion are partly visible behind the wheel *K*. The base is adjusted and locked in position by means of two set screws in the left hand end of each runner; they bear against studs screwed into *B* through oversized holes in the runners. This mounting is thus a sort of cantilever and permits a necessary adjustment of the axis of rotation of the crystal with respect to the rest of the instrument.

Two vertical posts, one of which is shown, bolt to the forward end of the sled and have bolted to their upper ends a steel cross piece *N*, which in turn carries the adjustable mounting for the slit S_2. In the center of the sled is a scraped seat, with a large hole bored through it, to which is bolted the bearing for rotating the crystal.

The parts *B*, *C*, *D*, *F*, *J*, and *M* are made of cast iron. After being machined, but before the final finishing was done, they were artificially aged. The aging process was apparently effective, for none of the parts has shown any noticeable warping during several years.

A section of the plate-holder *J* in a plane parallel to that of *XY* is shown at (*a*) in Fig. 4 in position on the carriage *F*, and in perspective with the cover partly removed at (*b*). The holder is supported and positioned by two cone-pointed bolts, one of which is shown at *T*, and the round-ended screw *U*. The cone points fit in the slot milled across the steel plate which is bolted to *F*, and the screw *U* bears against a plane surface milled on *F*. The cone of one of the bolts is not coaxial with the bolt, thus permitting a small rotation of the plate-holder about a vertical axis. Adjustment about the line of the slot is made with the screw *U*. The center of gravity of the plate-holder is far enough forward of the screws *T* to keep the holder in position when the carriage is moved. The plate-holder is so compact that the distance from the center of the plate to the surface of the track below is only about 5.5 cm.

The plate-holder is of special design to ensure the flatness of the sensitized surface of the photographic plate. This surface is forced against two parallel flat surfaces on the cover, just to the left of *OO*, by thin walled rubber tubes *RR'* inflated with air at about two atmospheres pressure. The two surfaces *OO* are an integral part of a sufficiently large body of cast iron to prevent bending under this stress.

The cover of the plate-holder is one casting in the form of two *V*-sections joined together at both ends; these are reenforced by seven cross webs on each side, which terminate in bosses through which the fourteen screws *QQ* hold the cover to the back. Each of the *V*-sections is of the nature of a cantilever, such that the pressure on the surfaces *OO* causes a tension in the screws *QQ* and a pressure across the surfaces of contact between the cover and back of the plate-holder at *PP*. The back of the plate-holder offers about five centimeters depth of cast iron to resist both these stresses. The opposing surfaces of the cover and back, as well as the surfaces *OO*, were scraped plane to a high degree of precision. It had been the original intention of the designer to finish these surfaces by lapping, but it was feared that the slight peening action of the abrasive would only warp them. The edges of the sur-

faces were left sharp so that in working the two parts of the holder into contact dust particles would be removed.

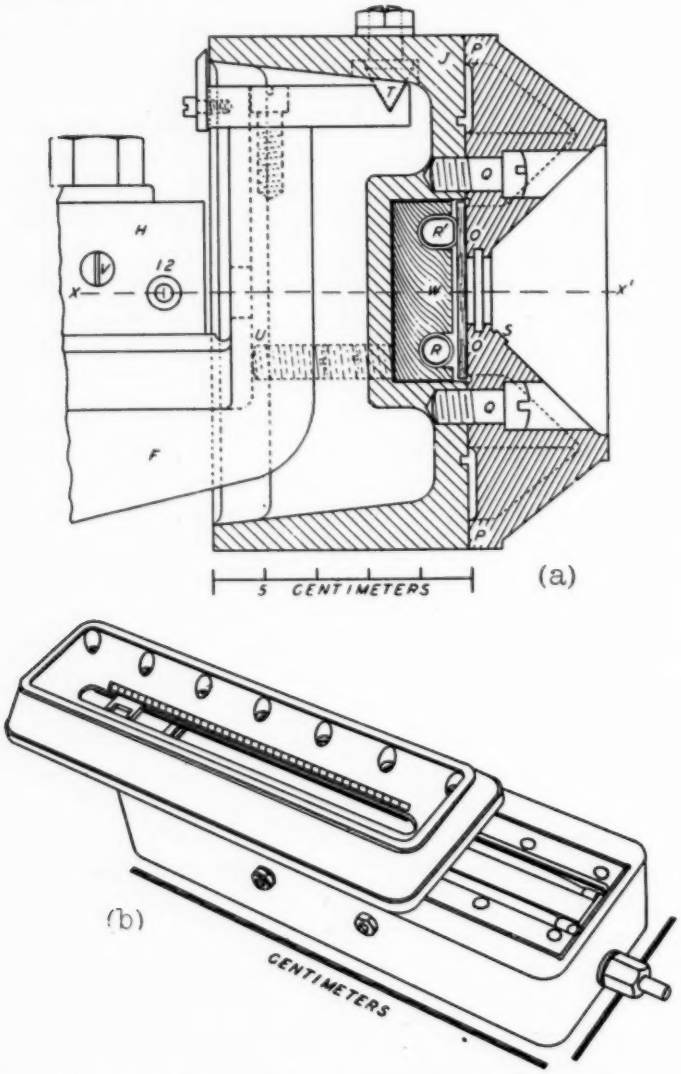

Fig. 4. Cross-section and perspective of plate-holder.

A strip of black paper, fitted into slots in the *V*-sections, covers the opening between the sections and serves as a light seal. A centimeter scale, ruled on the surface *S* along one side of the opening, facilitates the positioning of a lead screen when it is desired to shield a portion of the plate from x-rays. The photographic plates were cut in strips 25 cm long and 3.4 cm wide, dimensions such that the extreme edges of the strips extended slightly beyond the boundaries of the surfaces *OO*. This was to prevent irregularities in the edges of the gelatin from interfering with the proper seating of the plate.

The mahogany strip W, backed by a piece of velvet, and having two longitudinal grooves 6 mm wide milled in its front, affords support for the rubber tubes and distributes the pressure in them uniformly to the back of the plate-holder. The portions of the rubber tubes which press against the photographic plate are thinner than the remainder. We are indebted to Mr. G. W. Patterson of the Seamless Rubber Co. of this city for these tubes. Air is admitted to the tubes through a nozzle shown just below the letter J, Fig. 2. The tube R' is shown inflated in the section. When the tubes are deflated. There is ample clearance between the plate and the surfaces OO to prevent scratching of the gelatin while the cover is being worked into place. The plate-holder assemblage weighs 5.6 kg.

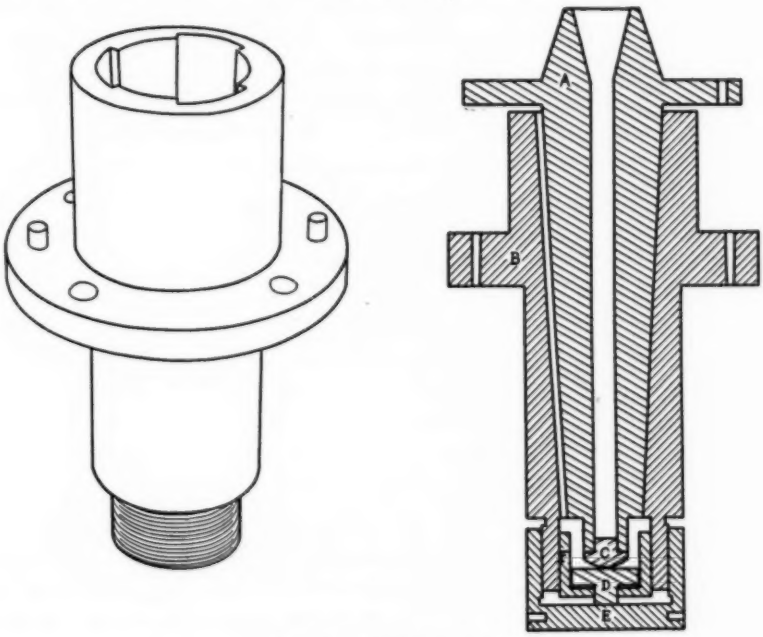

Fig. 5. Cone bearing.

The cone bearing for rotating the crystal is shown in Fig. 5. The flange on the seasoned cast iron sleeve B was scraped to fit its supporting seat on base C, Fig. 2, and the sleeve passes through the hole in this seat. The steel spindle A is a right circular cone supported by a hardened steel foot C; the lower surface of C is spherical and rests on the upper plane surface of D, also of hardened steel. The lower part of D is a stud which fits tightly in the sleeve F, and the latter has a sliding fit in B and a long enough bearing to keep D from rocking. The stud rests on the screw cap E, which is threaded to B with a fine thread and serves to adjust the bearing. By using a long tommy in the holes provided in E, the spindle and all its superstructure can easily be raised by as little as 2.5μ at a time. As the tangent of the semi-apical angle of the cone is slightly less than 0.06, an accurate means is at hand for adjusting the oil film separating the surfaces of A and B to the minimum thickness required for

lubrication. If this adjustment was correctly made at one angular position of the cone, it was found to be correct for all others, showing that the cone and its bearing fitted accurately. This corroborated what had already been inferred from the usual test with prussian blue. When the spindle was properly adjusted, a diminution in the thickness of the oil film of 0.3μ would cause the oil to cease acting as a lubricant. Therefore the cone may be considered to rotate in B about a practically *fixed* axis.

An essential feature of the design of the sleeve B is that portions of its bearing surfaces are relieved to insure the proper distribution of the oil and to prevent particles of foreign matter from getting between the bearing surfaces. This is done by removing one half the bearing area of B by three grooves, similar to rifling, but running parallel to the elements of the cone. The edges of these grooves were left sharp. This bearing was originally set up four years ago with "3 in 1" oil for lubricant, and the above tests and adjustment made. Since that time, no oil has been added, nor has any adjustment been found necessary by later tests. The oil shows no sign of having evaporated, or of becoming sticky after lying idle for six months at a stretch. It is doubtful if expensive watch oil would have been more satisfactory. If such a bearing was being built for continuous use, it would be well to replace the steel bearing surface of D by one of agate.

The spindle A is bolted to the divided circle table L, Fig. 2, and can be rotated by a tangent screw, the divided head of which appears at K in the figure. Screwed to the upper surface of this table and coaxial with it, is a circular brass plate with three radial slots 120° apart which serve to position the crystal holder or an auxiliary slit.

The bilateral slits, S_1 and S_2, have gold jaws 2.4 mm thick, 2.5 mm wide, and 1 cm high, inserted in brass plates which slide in dovetails on the slit frames. The opposing surfaces of the jaws were carefully scraped flat. The slit widths can be varied by means of cams acting above their centers; but during the taking of spectrograms one jaw of each slit is held in place by two dowel pins, and the other jaw is clamped tight against platinum shims placed between the opposing surfaces above and below the limited portion of the slit used. The slit S_2 is at a fixed height above the supporting bar N, but S_1 can be raised or lowered. Both slits can be rotated about horizontal axes through their centers and about vertical axes, and can be translated at right angles to the plane XY.

The crystal holder assemblage is shown mounted on the table L. Its base is a brass disk with three cone feet which fit the slots provided for it. On this base is mounted a rectangular plate with lateral adjustment. The plate supports, in a vertical sleeve with locking set screw, a sliding post which carries at its upper end the outer of a pair of coaxial cylinders. The inner cylinder can be rotated with respect to the outer by a tangent screw. The crystal is fixed by soft wax with its working face against the surface of a slotted brass plate, which bolts inside the inner cylinder in such a manner that the axis of the latter lies approximately in the face of the crystal. Thus, the lateral and rotational adjustments of the crystal are independent. The

crystal holder can be replaced by an auxiliary slit (not shown) later referred to as S_3. The later is so adjusted that, when in place, its long axis coincides with the axis of rotation Y, and the plane through its upper corners contains the axis XX'.

The x-ray tube is mounted on a bakelite stand in a rectangular box of 5 mm lead sheet. The box is supported on two pieces of channel steel 31 cm deep which rest on the same pier as the spectrometer. The tube used in these experiments was entirely constructed in this laboratory and was of Coolidge type with 15 cm bulb. The target was a button of silver welded, to insure good thermal contact, to a water-cooled copper anode. The x-rays were taken at an angle of about 3.5° to the plane of the target. The cathode, heated by current from a storage battery, was designed to bring the cathode rays to an approximately line focus on the target. With this in view, the filament was wound in a spiral groove on a tapered mandrel, just as for a fine focus Coolidge filament; but, instead of being annealed between spherical surfaces, it was placed between cylindrical surfaces of 19 mm radius during annealing. This gave a focal spot on the target which was longer in one direction than in a direction at right angles; but, due to the magnetic field of the heating current, its long axis was inclined at an angle (roughly 45°) to the axis of the cylindrical filament. This is a drawback if it is desired to change the strength of the filament current after the tube has once been aligned with respect to the spectrometer. We hope to overcome this difficulty by the use of a non-inductive filament. Such a filament should have a greater thermionic emission at its center, owing to the elimination of the center lead, and should give an excellent focal spot distribution. We have succeeded in winding such a double filament, but have not had an opportunity to mount and try it.

The cooling water was circulated by a pump through a Ford automobile radiator and its temperature measured just before and just after passing through the anode. By regulating the speed of a fan blowing on the radiator, the temperature, and therefore the length of the anode could be held constant, thus keeping the focal spot on the line through the narrow slits used.

The source of potential for the tube was a 10 K.V.A. transformer connected to the 220 volt, 60 cycle, city supply. It was controlled by a variable inductive reactance in the primary and had a mechanical rectifier in the secondary, utilizing about one half of each side of the wave.

For precision measurements with the above described apparatus, it is essential that the plate-holder, when the carriage F is moved along its ways, should have rectilinear motion only; and that there should be no appreciable motion of the microscope relative to the crystal. It is also important to have the planes of the opposing faces of the slit jaws parallel to the plane XY, and the reflecting planes of the crystal approximately parallel to the axis of rotation. These adjustments were made with the aid of several steel mirrors of different thickness, each having two opposite reflecting surfaces accurately plane and parallel; and an auto-collimating device for detecting and measuring any rotation of the mirrors. The auto-collimator consisted of a 43 cm focal length objective with illuminated cross-hairs in its focal plane. The

90° cross-hairs, together with their reflected image, were viewed with a 20-power micrometer microscope. The sensitivity of this arrangement was 7, micrometer divisions per second of rotation of the mirror, and one-third of this rotation could be detected. For detecting small motions of one part of the spectrometer relative to another, two steel balls were fastened to one part, a third ball to another, and on a glass or hardened steel plate resting on these three balls was mounted a mirror facing the auto-collimator. When the balls bore on hardened surfaces, scrupulously clean, a relative motion of 0.01μ could be detected by this device.

Making use of this tilting mirror, it was found that the largest relative motion between the spectrometer microscope and the axis Y, due to moving the carriage F with the plate-holder along the ways, was the entirely negligible amount of 0.06μ. The carriage, when displaced the full length of the ways, rotated about horizontal and vertical axes perpendicular to its line of motion by the insignificant amounts of one and two seconds respectively, as measured with the auto-collimator. A sensitive spirit level showed no greater rotation abouts its line of motion.

These tests having been made, the sled C was adjusted, with the aid of the auto-collimator and mirrors until the Y-axis was perpendicular to XX'. A micrometer microscope, giving 45° deviation, was then clamped to the carriage F and adjusted until the axis of its objective coincided with the line XX', thus supplying a means for bringing the centers of the slits S_1 and S_2 into this line.

The measuring bar was adjusted by a dial indicator until the scraped surface on the side opposite the plugs was parallel to XX' to within 3 seconds of arc. Since the surfaces of the plugs had all been ground and polished into one plane parallel to this scraped surface, this adjustment brought their surfaces parallel to XX', and insured all of the diamond scratches being in focus without parallax as they came opposite the microscope, once this was focused on one of them.

By means of a mirror wrung to the vertical scraped surface of H, another on the divided circle table with its surfaces parallel to the axis Y, and mirrors clamped between the jaws of the slits S_1 and S_2, the auto-collimator could be set with its axis normal to the plane XY, and the slits adjusted until the surfaces of their mirrors were parallel to this plane. The slit surfaces were thus adjusted parallel to Y within 30″ and to XX' within 15″. In a similar manner the plate-holder was adjusted so that the plane of the photographic plate would be approximately perpendicular to the axis XX'. The crystal, which had a cleavage face giving fair optical reflection, was similarly adjusted so that this face was parallel to the axis Y and as nearly as possible in this axis, the latter adjustment being made with a high power microscope. The various mirrors were brought opposite the auto-collimator by sliding the carriage B, and slit bracket M along the tracks on A. Wherever possible, the foregoing tests were checked with a spirit level sensitive to 5 seconds of arc per mm displacement of the bubble and, in some cases, with one of five times this sensitivity.

The greatest care was used to test the flatness of the opposing surfaces of the two parts of the plate-holder, not only when the plate-holder was disassembled and free from stress, but also when it was assembled and the air pressure applied.

The front portion, mounted on the carriage *F* in such a manner that it could be moved parallel to the surfaces *OO*, was examined with an interferometer using parallel and approximately monochromatic green light. The high portions of the scraping marks on these surfaces were so nearly continuous, and so well polished from working the two parts of the plate-holder together during assemblage, that the fringes were entirely unambiguous and could be counted. After allowing for the slight departure of the motion of *F* from a straight line, the surfaces *OO* were found to be flat to one fringe.*

The back of the plate-holder was similarly mounted on the carriage *F*, but the scraping marks were not close enough together to give useful fringes. However, with mirrors wrung to its surfaces in various places, it was tested both with the interferometer and the auto-collimator, and no evidence of an appreciable deviation from flatness was observed. This, together with the usual test for the fit of two scraped surfaces, convinced us that these surfaces were flat enough when separate and not under stress. Incidentally, the rectilinear motion of the carriage *F* was checked when these observations were made.

The plate-holder was then assembled with a photographic plate of "parallel plate" glass 1.5 mm thick in place. Tilting mirrors with short lever arms showed that contact between the surfaces *OO* and the gelatin surface was approximately complete at a pressure of 25 lb in^{-2}, because an increase to 30 did not diminish the separation of these surfaces by as much as 0.1μ. A pressure of 12 was required to expand the rubber tubes. The photographic plate was then replaced by a strip of "parallel plate" glass of the same thickness, without gelatin, and this was examined with the interferometer, the air pressures varying from 20 to 30. The fringe system showed very little change after a pressure of 25 was reached, showing approximately complete contact at this pressure. Though the surface of "parallel plate" glass is not optically perfect, the interferometer could be set so that there were not more than one or two fringes in a distance of 3 cm at any part of the strip. The number of fringes per cm was determined for every centimeter of the useful length of the plate, as the plate holder moved parallel to the plane *OO* in front of the interferometer. This procedure was repeated with several other strips of "parallel plate." The data thus obtained gave no indication of a curvature of the surfaces *OO* which could cause a constant error in measurements of glancing-angles of as much as 0.04″. The gelatin surface of ordinary commercial photographic plates, when examined with the interferometer, showed very rapidly changing local curvatures many times greater than any constant curvature that could be introduced by the plate-holder. It is in-

* The perfection of the spectrometer and plate holder is largely due to the painstaking care with which the scraped surfaces were fitted by Mr. Moody of the Pratt and Whitney Company.

teresting to note, in this connection, that when a strip of gelatin was removed from the plate, the fringe system associated with the remaining gelatin was usually continuous with that associated with the glass. This showed that the upper surface of the gelatin conformed pretty generally to the irregularities of the glass surface on which it was coated.

The spectrometer, having been adjusted and tested in the manner described, was next aligned with the source of x-rays. In order to obtain maximum intensity through two very narrow slits, it is necessary that the line of centers of the slits should pass through the center of the most intense region of the focal spot on the target. As the authors have previously shown,[5] the focal spot is striated when the hot cathode is a spiral filament, being approximately a projection of the turns of the filament on the target. By taking x-ray photographs through S_1 when S_3 was in place and again through horizontal slits substituted for S_1 and S_2, it was possible to adjust the tube and spectrometer so that the latter was approximately level, and the center line of S_1 and S_2 passed through the center of the most intense region of the focal spot. That this line coincided with the axis XX', as previously defined, was also checked photographically with the aid of S_3.

Part III. Experimental Procedure

The crystal used was a calcite rhomb $12\times10\times7$ mm cleaved from a block of Iceland spar obtained from the "Marsh Collection," Yale University. This specimen is denoted by Ca 1. The largest cleavage face was used for reflection, and, as far as could be found by examinations with reflected light and with a microscope, the portion on which the x-rays fell was a plane. After mounting in the crystal holder with soft wax, this face was adjusted parallel to, and into coincidence with, the axis of rotation within 25″ and 10μ respectively. A tilt of 25″ would cause an error in the glancing angle under consideration of 0.0004″.

Due to refraction, no crystal is a perfectly selective reflector, and therefore a monochromatic beam, upon reflection, will diverge beyond the limits of the rectangular region discussed by Uhler.[2] A sufficient measure of this divergence was obtained, without using a double crystal method, by comparing the angular width of the incident beam, as calculated from the slit widths, with the angle through which the crystal could be turned while still reflecting some energy of the wave-length under consideration. The limits of this angle were determined by finding the angular settings at which the crystal ceased to give an image on the photographic plate, during an exposure time a little too short to permit the formation of a perceptible image due to white radiation. This angle was approximately 46.8″, with an extreme variation of less than 10 percent. As the beam was limited by the slits to an angular width of 26″, the divergence due to the crystal was 20.8.″

Table I gives a comparison between line widths calculated from the above angle and average line widths measured on the spectrograms, at three different distances from the crystal denoted by the plug numbers on the mea-

[5] C. D. Cooksey and D. Cooksey, Science **58**, 382 (1926).

suring bar. The plate intersected the reflected beam near the Bragg focus of S_2 and S_1 in the first and third positions respectively and about half way between these foci in the second position. Considering the difficulty of de-

TABLE I. *Line widths at various positions of plate.*

Plug No.	0	6	11
Calculated	0.0249 mm	0.0400 mm	0.0535 mm
Measured	0.0276 "	0.0395 "	0.0519 "

termining line widths, the above figures are in fair agreement and give a reasonable indication of the perfection of the crystal. In practice it was found that a properly filled out image was obtained when the crystal was rotated through an angle of 18″ symmetrically about the best setting; no additional width accrued due to energy from the wave-length under investigation through using a larger angle.

Uhler[2] has pointed out that oblique rays in a plane parallel to the axis of rotation of the crystal broaden the image asymmetrically. During the taking of spectrograms, the incident beam was limited by the following conditions: the widths of the two slits S_1 and S_2 were fixed by strips of platinum foil 0.02 mm thick, their lengths were limited to 3.2 and 2.5 mm respectively, and their distances from the crystal were 35.5 and 4.5 cm respectively. Limited thus, the maximum effect of oblique rays on the glancing-angle is the negligible amount of 0.02″ for an eleven inch displacement.

In order to reduce the values of the glancing-angle obtained from the spectrograms to their values at a standard temperature, it is necessary to know the coefficient of expansion of calcite along the normal to its cleavage planes; i.e., the coefficient a_{18} in the formula $\sin\theta_{18}=\sin\theta_t[1+a_{18}(t-18)]$. W. Stenström[6] gives the generally quoted approximate value of $1.04(10)^{-5}$ per degree centigrade, which is not precise enough to be used to correct data of the accuracy attained today. In obtaining this value, he assumed an angle of 45° between the optic axis and the normal to a cleavage plane, and $2.62(10)^{-5}$ and $-0.54(10)^{-5}$ per degree centigrade respectively for the coefficients parallel and perpendicular to the optic axis. We have recalculated the coefficient using the following constants: the axial angle of the crystal is 101° 55.0′ ±0.2′ at 22°C as given by H. N. Beets;[7] the mean coefficients of expansion parallel and perpendicular to the optic axis are $(\alpha_\parallel+2\,\beta_\parallel t)$ and $(\alpha_\perp+2\,\beta_\perp t)$ respectively where:

$$\alpha_\parallel=+2.513\ 53\ (10)^{-5} \qquad \beta_\parallel=+0.001\ 18\ \ (10)^{-5}$$
$$\alpha_\perp=-0.557\ 82\ (10)^{-5} \qquad \beta_\perp=+0.000\ 138\ (10)^{-5}$$

in degrees centigrade as given by Benoît.[8] The value of the coefficient a_{18} corresponding to these constants is:

[6] W. Stenström, Dissertation, Lund (1919) p. 38.

[7] H. N. Beets, Phys. Rev. [2] **25**, 621 (1925).

[8] R. Benoît, Travaux et Memoires du Bureau International des Poids et Mesures **6**, 190 (1888).

$$a_{18} = 1.02_3(10)^{-5},^{1}$$

which, if used over a sixteen degree interval, will give the correction of the glancing-angle for the $K\alpha_1$ line of sliver to 18°C within 0.008″.

Table II gives $\log_{10}[1+a_{18}\ (t-18)]$ for the interval 10°C to 26°C.

TABLE II. *Temperature correction for calcite.*

t°C	log $[1+a_{18}(t-18)]$	t°C	log $[1+a_{18}(t-18)]$
10	0.999 964 46	18	0.000 000 00
11	968 90	19	004 44
12	973 34	20	008 88
13	977 79	21	013 32
14	982 23	22	017 76
15	986 67	23	022 21
16	991 12	24	026 65
17	995 56	25	031 09
18	0.000 000 00	26	035 53

A Gaertner measuring engine was used to measure the spectrograms and the distances between the fiducial lines on the measuring bar. The pitch of the screw is approximately 0.5 mm, and the least count of the divided head is 1μ. The errors of the screw were investigated by measuring, on successive parts of the screw, two overlapping 9 mm distances between fine lines on a glass plate manufactured by the Zeiss Company. As both these distances were within less than two divisions of a whole number of turns at all stations, errors of one turn did not enter. The settings were determined with parallel hairs in the eye piece of a three hundred power microscope. The algebraic sums of the residuals from the mean of the 9 mm lengths for successive intervals were plotted against the corresponding 9 mm stations on the screw. The errors so determined all lay within 0.1μ of a smooth curve. The errors in one turn were found at four stations, equally distributed along the screw, by measuring a 0.1 mm interval on the glass plate for successive fifths of the head. These errors are nearly sinusoidal and therefore are eliminated in the mean of three measurements started from three stations on the head, each of which is separated from the others by one third of a turn. As only relative linear measurements are involved in the displacement method, an absolute calibration of the screw was not made, although its units are termed millimeters throughout this paper.

For comparing the measuring bar with the screw the spectrometer microscope was used. The reliability of setting on the lines was found from the maximum variation between settings occurring in each of 143 groups, each group consisting of two to four settings on a line. The maximum variation of setting in one group was 0.9μ, and the average about 0.25μ. Table III gives the frequency of occurrence of the variations of different amount, from 0.1μ to the maximum, for all the groups.

TABLE III. *Frequency of occurrence of large and small variations in setting.*

Frequency of occurrence of a certain variation	25	28	35	23	14	6	8	1	1	2	0
Amount of variation in a group μ	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.0

The maximum amount that any setting differed from the mean in any of the 143 groups was 0.5μ. Thus it appears that, when the plate-holder is displaced by a certain interval on the bar, the chance will be very small that the actual displacement will differ from the measured value of the interval by as much as 1μ, in spite of the fact that the end positions of the interval are determined only once. Such an error in the displacement would cause an error of 0.07″ in the glancing-angle under consideration.

The following procedure was adopted for obtaining spectrograms. 8×10 plates were cut in strips of the correct size and "*normalized*,"* the edge strips being discarded; after drying, the edges of the gelatin were carefully bevelled by cutting with a sharp knife blade, inclined at a slight angle with the plane of the plate, to remove irregular frills. A plate having been placed in the plate-holder, and the rubber tubes inflated, the holder was mounted on its carriage, with a lead screen so placed as to shield the plate from the lower half of the direct beam. Then the carriage was moved to that one of the desired positions which was most remote from the crystal and adjusted until, when locked, the setting of the microscope cross-hairs on the corresponding fiducial line of the bar appeared exact. After the lapse of at least twelve hours, the setting of the microscope was again scrutinized, but in no case was it necessary to readjust it.

With thermal equilibrium thus assured, the spectrogram was taken. First, with the divided circle set so that the crystal holder did not intercept the incident beam, a short exposure was made to record the upper half of the central image. Then the spectral line was taken on both sides of the direct beam, equal exposures being given for each of five angular positions of the crystal symmetrically spaced about the best setting on each side and covering a range of 18″; this was repeated for each desired position of the plate-holder. The tangent screw was disengaged from the circle table before making an exposure to avoid unnecessary stress on the cone bearing, and the microscope setting was checked before and after the set of exposures for each spectral image. During each exposure, the temperature of the crystal was recorded from the reading on a calibrated mercury thermometer having five divisions per degree centigrade; this thermometer was so held by a clamp that its bulb was three centimeters from the crystal. After the last spectral image exposure the plate-holder was moved (when necessary) to that station which had been nearest the crystal, and a short exposure was made for the central image with the lead screen moved, and the crystal turned so as not to interfere with the direct beam. The plate-holder was then given a small transverse displacement, and the central image again taken for convenience in measuring the separation of the portions of the central images taken with the holder in its two extreme positions.

During exposures, the current through the x-ray tube was approximately 4 m.a.; and the filament current was regulated so as to maintain a brush

* By *normalizing* we mean soaking the unexposed plate in water for thirty minutes, then in strong ethyl alcohol for twenty minutes and finally leaving it to attain equilibrium in a humid atmosphere. The reasons for subjecting the plates to this process are fully discussed in another paper.[14]

discharge, with only occasional sparking, between the blunt points of a six inch spark gap in parallel with the tube. No attempt was made to get a more exact measure of the potential, but these operating conditions assured spectral images of ample density with exposures of moderate duration.

Table IV gives the detailed data recorded during the taking of a typical spectrogram, plate AG2, and Fig. 6 is a drawing to scale of this spectrogram.

TABLE IV. *Typical exposure record.*

Plate AG2. Line Ag $K\alpha_1$. Crystal Ca 1. S_1—axis 35.5 cm. Plate—axis 32.7, 4.8, and 20 cm. S_1 and S_2—0.02 mm. Spark gap 6 in. Tube current 4 m.a. Rheostat button 3. Filament current 3.7 amps. Set up 5 P.M. May 3, 1928. Exposures started May 4, 9:15 A.M., finished 11:45 A.M.

Exp. No.	Micr. set on plug	Crystal setting Deg.	Crystal setting Div.	Temperature Crystal °C	Temperature Anode °C	Air pressure plate-holder lb./sq. in.	Exp. time min.
1	11	out*					2
		343.0	6.0	24.7	28.0	27.2	6
		"	7.0	24.7	27.2		6
2	11	"	8.0	24.7	29.0		6
		"	9.0	24.9	28.2		6
		"	10.0	24.9	28.0	27.2	6
		152.0	439.0	25.0	28.0	27.1	6
		"	440.0	25.1	28.0		6
3	11	"	441.0	25.1	28.0		6
		"	442.0	25.2	28.1		6
		"	443.0	25.2	28.1	27.0	6
		152.0	439.0	25.3	27.8	27.0	3
		"	440.0	25.2	27.4		3
4	0	"	441.0	25.3	27.7		3
		"	442.0	25.3	28.0		3
		"	443.0	25.3	28.1	26.9	3
		343.0	6.0	25.3	28.1	26.9	3
		"	7.0	25.4	28.0		3
5	0	"	8.0	25.4	28.1		3
		"	9.0	25.4	28.2		3
		"	10.0	25.4	28.3	26.9	3
		343.0	6.0	25.5	28.2	26.9	5
		"	7.0	25.5	27.9		5
6	6	"	8.0	25.5	28.2		5
		"	9.0	25.5	28.3		5
		"	10.0	25.6	28.5	26.9	5
		152.0	439.0	25.6	28.6	26.9	5
		"	440.0	25.6	28.5		5
7	6	"	441.0	25.6	28.7		5
		"	442.0	25.6	28.7		5
		"	443.0	25.7	28.8	26.6	5
8	0	out*					1
9	0	out* (plate-holder displaced sideways 2 mm)					1

Remarks: Developed 4 min at 77°F, fixed 20 min, washed 30 min, rinsed in distilled water 10 min, and soaked in alcohol 20 min at 77°F, then dried in a humid atmosphere.

* Turned to give direct transmission.

After the plates were thoroughly dry, rulings were scribed at intervals on the gelatin surface (the dotted lines in Fig. 6) along a line through the centers of, and normal to, the spectral images, and all measurements were made along this line except those of the central image separation. If the spectral images were not filled out and black, they were discarded. Table

TABLE V. *Plate* AG2. *Engine settings in millimeters.*

	Top Up			Top Down		
A	162.2487	162.0819	161.9182	23.7314	23.5627	23.4006
	92	.0793	89	.7270	20	.3982
	78	.0809	67	.7290	26	.4004
Mean	162.2486 (20.2°C)	162.0807 (20.0°C)	161.9179 (20.0°C)	23.7291 (20.0°C)	23.5624 (20.4°C)	23.3997 (20.2°C)
B	138.5332	138.3640	138.1996	47.4476	47.2782	47.1170
	14	50	.2004	78	95	57
	33	48	.2000	93	89	63
Mean	138.5326 (20.1°C)	138.3646 (20.0°C)	138.2000 (20.0°C)	47.4482 (20.0°C)	47.2789 (20.2°C)	47.1163 (20.2°C)
C	110.0780	109.9086	109.7470	75.9033	75.7361	75.5720
	64	.9104	84	40	61	13
	77	.9104	76	28	41	16
Mean	110.0774	109.9098 (20.1°C)	109.7477 (19.8°C)	75.9034 (20.1°C)	75.7354 (20.4°C)	75.5716 (20.3°C)
D	92.1552	91.9880	91.8245	93.8269	93.6567	93.4956
	69	74	40	78	84	52
	55	78	51	70	79	56
Mean	92.1559 (19.9°C)	91.9877	91.8245 (19.8°C)	93.8272 (20.0°C)	93.6577 (20.4°C)	93.4955
E	63.7039	63.5360	63.3716	122.2768	122.1082	121.9471
	60	59	20	68	77	79
	59	60	29	88	81	80
Mean	63.7053 (19.8°C)	63.5360 (20.2°C)	63.3722 (19.6°C)	122.2775 (20.2°C)	122.1080 (20.4°C)	121.9477 (20.4°C)
F	39.9994	39.8311	39.6623	145.9828	145.8144	145.6543
	90	18	37	10	66	.6498
	70	03	48	12	31	.6523
Mean	39.9985 (19.6°C)	39.8311 (20.2°C)	39.6636 (19.6°C)	145.9817 (20.4°C)	145.8147 (20.4°C)	145.6521 (20.4°C)
L	102.8114	102.6425	102.4800	83.1689	83.0037	82.8415
				.1710		
Mean	102.8114	102.6425	102.4800	83.1699	83.0037	82.8415
N	101.1121	100.9447	100.7813	84.8668	84.7000	84.5386
				86		
Mean	101.1121	100.9447	100.7813	84.8677	84.7000	84.5386
L	108.1553	107.9860	107.8243	82.8453	82.6748	82.5122
M	106.4640	106.2956	106.1320	84.5346	84.3655	84.2016

V gives the details of the measurements of the spectrogram illustrated. Before the value of the glancing-angle can be computed, the measured distances must be increased by the following quantities: $a \equiv$screw correction; $b \equiv$correction for difference between temperatures of plate when taken and

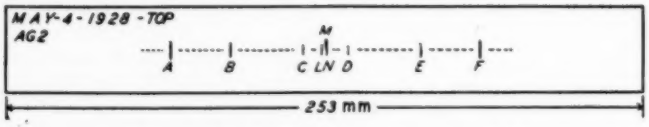

Fig. 6. Facsimile of spectrogram AG2.

when measured; $c \equiv$lateral shift of plate-holder during displacemnte as indicated by central image separation. These corrections together with the corrected values of the distances between spectral images and their corresponding displacements are given in Table VI. The values of the angle

TABLE VI. *Plate* AG2. *Corrections to measurements.*

Distance Fig. 6		$a\times$ $(10)^4$mm	Mean Temp. Diff. δ°C	$b\times$ $(10)^4$mm	$c\times$ $(10)^4$mm	Image separation corrected	Displacement mm
A-C	Up	+6.8	5.05	−9.7	−73	52.16406	279.44590 ±0.00042
	Down	+0.7					
D-F	Up	+1.3	5.05	−9.7	+73	52.16378	
	Down	+4.7					
B-C	Up	+4.0	5.35	−5.6	−40	28.45062	152.42506 ±0.00020
	Down	+1.6					
D-E	Up	+0.3	5.35	−5.6	+40	28.45471	
	Down	+1.0					

Differential thermal coefficient glass plate-screw 3.7 $(10)^{-6}$ per °C.

ω between the normal to the plate and the line XX', computed by Eq. (2) from the data corresponding to the two different displacements, differ in magnitude and sign; but the more precise optical tests had shown very conclusively that the maximum rotation of the plate-holder, for any displacement along the tracks, was less than $2''$. Such differences are, therefore, probably due to residual fortuitous variations in position of a developed image with respect to its corresponding latent image,[14] and the fact that commercial plates cannot be forced flat.

Table VII is given as an illustration of the accuracy with which the spectrograms could be measured. As shown in Table V, the distances be

[9] A. Leide, Dissertation, Lund (1925).
[10] A. P. Weber, Zeits. f. wiss. Photo. **23**, 149 (1925).
[11] K. Lang, Ann. d. Physik [4] **75**, 489 (1924).
[12] G. Kellström, Zeits. f. Physik **41**, 516 (1927).

tween pairs of lines were measured first with the plate in one position on the engine, and again when it was reversed ("top up", "top down"). The numbers tabulated are the differences between the means of these measurements in each position. The first three plates had lines corresponding to

TABLE VII. *Difference between measurements direct and reversed.*

Spectrogram	Differences		Spectrogram	Differences	
	11 in. displ.	6 in. displ.		11 in. displ.	6 in. displ.
AG1	0.25μ	0.29μ	AG3	0.56μ	0.04μ
AG2	0.20μ	0.44μ	AG4	0.81μ	

both 11 and 6 in. displacements, but the fourth had only the former. The measurements on plate AG4 were repeated. If the new measurements are averaged with the first set, the corresponding difference is 0.72 instead of 0.81μ. If it is assumed that the measurements can be in error by as much as 0.81μ in the case of the 11 in. displacement, the resulting glancing-angle would be in error by 0.29″. The maximum effect on this angle due to the uncertainty of setting on the bar is 0.07″. Therefore it seems evident that there is a negligible chance that values of the glancing-angle obtained from different 11 in. displacements can fluctuate, due to errors of measurement, by as much as 0.36″, assuming of course good lines on the spectrograms. Remeasurements made after a lapse of three months on another plate, AG5, by an independent observer gave glancing-angle values differing for the 5 and 6 in. displacements by 0.13″ and 0.00″ respectively.

TABLE VIII. *Effect of method of measurement. Plate No.* AG9, *4 in. displacement, taken at* 22.1° C. *glancing-angle at* 18° C.

Measured at ° C.	Uncorrected for temp. of meas.	Corrected for temp. of meas.	Description of method of measurement
20.5	5° 17′ 14.54″	5° 17′ 14.42″	Deep focus objective; 57° cross-hairs; 18 X.
21.2	5° 17′ 14.41″	5° 17′ 14.34″	Same objective; parallel hairs separated to straddle width of remote lines; 18 X.
19.7	5° 17′ 14.65″	5° 17′ 14.48″	Shallow focus; parallel hairs same; 20 X.
Remote 17.0 Near 19.0	5° 17′ 14.95″	5° 17′ 14.43″	Same objective, but parallel hairs suitably adjusted to measure separation of remote and near lines independently; 20 X.

Spectral images taken with the plate in a remote position are broader than those taken with it near the crystal; therefore, if parallel hairs of fixed separation are used in the measuring microscope, their adjustment will not

be suitable for both types of images. Plate AG9 was measured under varying conditions of magnification, type of eye-piece and temperature, and Table VIII gives the glancing-angles thus obtained. It will be observed that the second column shows excellent agreement for different methods of measurement, especially when it is borne in mind that for such a short displacement a variation in the image separation of 0.2μ would change the glancing-angle by $0.20''$, and that the near and remote lines were of different width.

Part IV. Results

The final results are given in Table IX. They were obtained from eight spectrograms, six of which were taken with the plate-holder in three, the remainder in only two, positions, but that nearest the crystal was the same for all. All the plates had been cut from the central portions of large plates; AG1 to AG4 from one Eastman "40," AG5 to AG7 from another, and AG9

Table IX. *Final data and results. Line*; Ag ($K\alpha_1$). *Crystal; Calcite* (Ca 1).

Spectrogram	Displ't inches	Taken at ° C	Glancing-angle at 18° C	Mean values, probable errors of mean and of one determination respectively
AG1	11	25.2	5° 17′ 13.68″	
" 2	11	25.1	14.00	θ=5° 17′ 13.79″
" 3	11	25.0	13.53	R= ±0.075
" 4	11	25.2	13.95	r= ±0.15
" 1	6	25.4	13.35	
" 2	6	25.4	13.78	
" 3	6	25.3	13.92	
" 5	6	21.4	13.03	θ=5° 17′ 13.82″
" 6	6	21.8	13.93	R= ±0.092
" 7	6	21.7	14.13	r= ±0.29
" 5	5	21.4	14.15	
" 6	5	21.7	13.43	
" 7	5	21.9	14.10	
" 9	4	22.1	14.42	

from an Eastman "Universal." If the values of the glancing-angle corresponding to eleven inch displacements are given twice the weight of the others, the following values are obtained:

$$\theta = 5°17'13.81''(\pm 0.06'') \text{ at } 18°C.^1$$

$$\lambda = 0.558238A^1(\log 2d_{18} = 0.7823350)$$

$$\pm 0.000002.$$

For comparison, the most reliable published results that we have seen are given with ours in Table X. In cases where the probable errors were not published we have calculated them from the data given. Omitting Kellström's second order value and weighting the others according to their probable errors,

$$\theta = 5°17'14.66''(\pm 0.036'') \text{ at } 18°C.$$

TABLE X. *Comparison with results of others.*

Orders used	Glancing-angle	Probable error of		Av. deviation from mean	Source
		Mean	One det'n		
1	5° 17′ 13.05″	0.4″	0.8″	1.0″	A. Leide[9]
1 & 2	7.8	0.7	2.0	2.2	A. P. Weber[10]
1	13.1	0.6	1.5	1.8	K. Lang[11]
1	15.2	0.045	0.12	0.13	
2	(10 37 9.8)	0.36	0.72	0.8	G. Kellström[12]
				11 in. displ't 0.2	
1	13.81	0.06	0.13		Present work
				Other displ't 0.34	

DISCUSSION

Of the values given in the table, Kellström's first order determination has the smallest probable error and is the one quoted in the International Critical Tables. The value he gives for the wave-length determined from second order reflection would predict a first order glancing-angle (5° 17′ 14.58″ ± 0.18″) approximately midway between his measured first order and ours and with four times his first order probable error. The fact that our value of the glancing-angle differs from his two values, and the latter differ among themselves, by about three times the sum of the respective probable errors would lead one to suspect that any one or all of the values may be affected by a constant error. From the point of view of agreement, the two sensibly identical values of Leide and Lang, large though their probable errors may be, favor our value rather than those of Kellström. The "Method of Displacement" may be subject to an error sufficient to account for our disagreement with Kellström's accepted value if the underlying assumption regarding the symmetry of the reflected beam is not fulfilled. However, the mean value of the glancing-angle computed from the eleven inch displacements only, where the plate was near a Bragg focus in both its positions, is sensibly the same as that from other displacements, where the plate intersected an intermediate portion of the beam in one position (Table IX). This fact confirms our belief that the reflected beam possessed the required symmetry, in spite of the fact that the crystal was not a perfectly selective reflector. The exhaustive tests to which the apparatus was subjected failed to show any defect which could cause an appreciable constant error. The only remaining source of such an error seems to be the crystal. The discrepancy between the results would be accounted for by a difference in grating space of seven parts in a hundred thousand between the crystals used. We have made use of only one specimen of Iceland spar while Kellström has used two (Pk 1 and Pk 2), although most of his data were obtained from Pk 1. He states that both crystals gave the same result within his limits of error. However, in the one case in which he used Pk 2 for a second order determination of the wave-length considered here his result is identical with that of our eleven inch displacements. We have been unable

to find any statement by Leide or Lang giving information concerning the particular specimens of calcite used by them. DeFoe and Compton[13] have measured the density of specimens of calcite, obtained from various sources, within a probable error of $(10)^{-4}$ gm cm^{-3}. They give values for two specimens from Iceland which differ by thirteen times this amount, indicating a real difference in density, even though they allow only half weight to the value for one of these specimens in computing the mean density of all the specimens. If all variations in density are reflected in differences of grating space, a difference in density of $6\times(10)^{-4}$ gm cm^{-3} (less than half that found by DeFoe and Compton) between Kellström's crystal and ours would be sufficient to account for the difference in the values of the glancing-angle under consideration. The discrepancy might therefore be explained in this way, though it is doubtful that the observed differences in density are really due to variations in grating space.

TABLE XI. *Average variations in measured values of glancing-angle due to various causes.*

Displacements	11 in.	6 in.	5 in.	4 in.
Average variations due to:				
Variations in setting on bar	0.03$_4$″	0.06″	0.07″	0.10″
Unflatness of gelatin	0.17	0.31	0.37	0.50
Motions of images after exposure if plates are:				
normalized	0.25	0.46	0.56	0.69
not normalized	1.00	1.84	2.24	2.76
Sum of average variations:				
If plates are:				
normalized	0.45	0.83	1.00	1.29
not normalized	1.20	2.21	2.68	3.36
Observed average variations	0.20	0.33	0.30	—
Observed maximum variations	0.47	1.10	0.72	—

It is of interest to consider the effect on the final result of various causes of uncertainty in the directly measured quantities. The average difference between successive settings on the bar was 0.25μ, therefore any displacement of the plate-holder is subject to an average uncertainty of 0.5μ from this cause. Irregularities in the surface of the gelatin would cause the effective displacement to differ from the actual. An interferometer investigation of the gelatin surface of the developed spectrograms, when held in the plate-holder, showed that these irregularities could cause an average error in the displacement of 2.5μ. Our work on the unreliability of position of photographic images[14] showed that the average error in the measured value of a fixed distance, as recorded on photographic plates, was 0.7μ when the plates had been normalized and 2.8μ when they had not. These errors, of course, include both the error of setting and that due to motion of the image. Though the images of the template slits[14] could be set on more accurately than

[13] O. K. DeFoe and A. H. Compton, Phys. Rev. [2] **25**, 618 (1925).

[14] D. Cooksey and C. D. Cooksey, Phys. Rev. preceding article.

spectral images, we shall assume that these figures include the average variations that might be expected in the remeasurement of a spectrogram. The effect of the average variation due to each of these causes on glancing-angle values, calculated for various displacements, is shown in Table XI.

These statistics not only emphasize the advisability of normalizing photographic plates before using them as accurate recorders of distances, but suggest that, even for small glancing-angles, the accuracy of the displacement method would be improved by the use of emulsions coated on good *plate* glass. With the accuracy of setting on spectral images limited as it is, there would seem to be no necessity for resorting to more accurate methods of measuring the displacement. Even though the apparatus is massive and so has a large thermal capacity, there is little doubt that better precautions for maintaining it at a constant temperature would have a beneficial effect. However, the manipulation in the present work was carried out with special reference to making the effects of temperature changes fortuitous.

In conclusion we wish to express our great appreciation of the encouraging and helpful interest shown, during the whole progress of this work, by Professor Uhler and Professor Emeritus Hastings of this department. We are also grateful to Dr. Albert W. Hull of the Research Staff of the General Electric Company for advice in connection with x-ray tubes and filaments, and to Professors McKeehan and Uhler for helpful suggestions in connection with the presentation of this investigation. In directing the construction and exhaustion of x-ray tubes, we have been greatly aided by experience gained in our long association with Mr. Alfred Greiner, formerly connected with this laboratory.

THE SPHERICALLY SYMMETRICAL FIELD IN THE UNIFIED THEORY

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Abstract

In this paper a systematic investigation of the spherically symmetrical statical field in Einstein's unified theory of the electromagnetic and gravitational fields is given. The investigation is carried through in two cases: with and without time symmetry. By a time symmetrical field we understand one whose Riemann interval is not altered by changing $+dt$ into $-dt$.

To begin with we develop a generalization of the formulas for parallel displacement and covariant affine differentiation in Einstein's geometry which enables us to introduce orthogonal transformations of the local coordinates, so as to bring them formally into agreement with the Gaussian coordinates. We then solve the Einstein field equations $F^{\mu\alpha}=0$ and $G^{\mu\alpha}=0$, first without the assumption of time symmetry. We determine the values and the physical significance of the constants of integration by considering the case of a very weak field, and obtain asymptotically the classical Coulomb field (e/r^2) and the classical Newtonian potential $(-m/r)$. Positive and negative electricity appear in the unified theory as given empirical facts, just as in the classical theory. In the present theory, however, the Newtonian field and the Coulomb field can be separated only asymptotically. In the immediate vicinity of a charged mass particle they are inextricably bound together.

Our solution gives a quadruple ("Vierbein")

$$ {}_1h^1 = 1 + e^2/r^4, \qquad {}_2h^2 = 1, \qquad {}_3h^3 = 1, $$
$$ {}_4h^1 = -(ie/r^2)(1 + e^2/r^4)^{1/2}, \qquad {}_4h^4 = 1 + m\int_r^\infty r^{-2}(1 + e^2/r^4)^{-3/2}dr. $$

All the other components vanish. By a transformation of variables this is shown to reduce to the quadruple recently calculated by Einstein and Mayer.

The field equations are then solved with the assumption of time symmetry. The electrostatic field vanishes, but the component g_{44} of the metric form has approximately the Schwarzschild value, while the others have the Euclidean values. Because of the absence of a law of motion, no observable predictions having to do with the path of an exploring particle can be made. It is shown, however, that in the unified field the theory gives in the first approximation the same red shift as the 1916 theory. If it is assumed that the orbit of a planet is a Riemannian geodesic, as in the 116 theory, then the advance of the perihelion of Mercury comes out approximately 7″ per century, that is, about the same as in the 1905 theory.

I. Introduction

A NUMBER of papers have recently appeared bearing on Einstein's attempt to construct a unified theory of the electromagnetic and the gravitational fields. The geometrical foundations of the new theory were laid down by Einstein in 1928,[1] without knowledge of the previous work of

[1] A. Einstein, Sitz. d. preuss. Akad. d. Wiss., 1928, p. 217; also Math. Ann. **102**, 685, (1930), hereafter referred to as "E.1." The reader is referred to this paper for explanation of the symbols and operations used in the present article.

Cartan and others on the same subject.[2] In a paper following immediately thereafter Einstein[3] suggested a unified field theory of the electromagnetic and gravitational fields in which the former was defined, in terms of the fundamental tensor h_σ^λ of a torsion geometry with distant parallelism, through an electromagnetic potential $\phi_\lambda = \Lambda_{\lambda\sigma}{}^\sigma$, where $2\Lambda_{\lambda\mu}{}^\sigma = h_\sigma{}^\sigma(h_{\lambda,\mu}{}^\sigma - h_{\mu,\lambda}{}^\sigma)$, and the latter through the usual gravitational potentials $g_{\mu\nu}$ defined in terms of the fundamental quantities $h_\lambda{}^\sigma$ by the relation $g_{\lambda\mu} = h_\lambda{}^\sigma h_{\sigma\mu}$. He further suggested a set of field equations for the determination of the tensor h_σ^λ, obtained from the variational equation

$$\delta \int h g^{\mu\nu} \Lambda_{\mu\beta}{}^\alpha \Lambda_{\nu\alpha}{}^\beta d\tau = 0. \tag{1}$$

The spherically symmetrical statical field in the unified theory was then investigated by Wiener and Vallarta.[4] In accordance with Einstein's definitions of the electric and gravitational fields, one had to expect that in the time symmetrical case one should obtain the Schwarzschild solution for the gravitational field of an uncharged mass particle, the Nordström-Jeffery solution[5] for the charged mass particle and, asymptotically the classical potential $\pm e/r$ for the electrostatic field. Instead they found that in this case, adopting Einstein's definition of the electromagnetic potential, the electrostatic field vanishes and, further, the gravitational field obtained by solving the field equations (1) also vanishes. One of the present authors[6] then pointed out that the vanishing of the electrostatic field is a consequence of the definition of the potential and has nothing to do with the particular choice of the field equations.

In 1929 Einstein modified his field equations several times. His first paper of that year[7] contains a second set of field equations which leads, as shown by Salkover[6], to the Schwarzschild solution for the gravitational field in the first approximation. In his second paper of that year Einstein[8] gave a third set of field equations based on a new Hamiltonian. Wiener, in an unpublished paper, was then able to show that this new Hamiltonian is, except for nonsignificant terms, precisely the Hamiltonian of the gravitational theory of 1916, and therefore leads to the gravitational field described by the Schwarzschild solution. Wiener also showed that Levi-Civita's[9] definition

[2] For a historical outline of the development of the Einstein geometry see a paper by E. Cartan, Math. Ann. **102**, 698, (1930).

[3] A. Einstein, Sitz. d. preuss. Akad. d. Wiss. 1928, p. 224.

[4] N. Wiener and M. S. Vallarta, Proc. Nat. Acad. **15**, 353, (1929), more specially Proc. Nat. Acad. **15**, 802 (1929).

[5] See for example Eddington's "Mathematical Theory of Relativity," p. 82 and p. 185, Cambridge, 1923.

[6] M. S. Vallarta, Proc. Nat. Acad. **15**, 784, (1929). The gravitational field obtained in this paper is vitiated by an error in transcribing the values of the electromagnetic potential from a previous paper by Wiener and Vallarta (footnote 4). The error was pointed out and corrected by M. Salkover, Phys. Rev. **35**, 209 and 214, (1930); acknowledgment by M. S. Vallarta, Phys. Rev. **35**, 435, (1930).

[7] A. Einstein, Sitz. d. preuss. Akad. d. Wiss. 1929, p. 2.

[8] A. Einstein, Sitz. d. preuss. Akad. d. Wiss. p. 156, 1929.

[9] T. Levi-Civita, Sitz. d. preuss. Akad. d. Wiss. p. 137, 1929.

of the electric vector leads to a vanishing spherically symmetrical, time symmetrical electrostatic field.

The development of the theory entered a new phase with Einstein's 1930 papers. Giving up the previous attempt to describe the electromagnetic field in terms of a potential ϕ_μ and also, as it appears, the description of the gravitational field in terms of the potentials $g_{\mu\nu}$, except in the case of a weak field, he suggested a fourth set of field equations to determine the fundamental tensor h_σ^λ.[10] The present paper is concerned with the solution of these field equations in the spherically symmetrical case, with and without time symmetry. It will be shown that the former case leads to a vanishing electrostatic field, while the latter gives, asymptotically, the classical Coulomb field. We believe this is the first instance where the asymmetry of past and future has played a fundamental role in a *field* theory. Positive and negative electricity appear in the unified theory as *given* empirical facts, just as in classical theory. Both cases, with and without time symmetry, give asymptotically the classical Newtonian potential. By making a suitable transformation of variables we show that the quadruple ("Vierbein") obtained without the assumption of time symmetry is identical with that found by Einstein and Mayer[11] by a different method.

Comparison with experimental evidence having to do with the motion of an exploring particle is impossible at the present stage, because the law of motion has not yet been discovered, but it may be conjectured on the basis of our present results that the path of an uncharged exploring particle in the pure gravitational field is not a geodesic with respect to the Riemannian ds^2 as in the 1916 theory. However, the unified theory leads to predict a shift of spectral lines towards the red which in the first approximation agrees with that of the 1916 theory.

II. Mathematical Introduction

In problems involving spherical symmetry it is usually found that a considerable simplification is achieved if spherical space coordinates r, ϕ, θ are used to locate a point in the field. In the Einstein geometry as formulated by him this immediately leads to a difficulty, because he does not allow orthogonal transformations of the local quadruples ("Vierbeine") so that locally and at each point the local coordinates may formally be made to agree with the Gaussian coordinates. If local orthogonal transformations are made use of certain formal generalizations are necessary which we now proceed to establish.

Let $g_{\alpha\beta}$ and γ_{ab} be the fundamental metric tensors in the Gaussian and in the local (Euclidean or pseudo-Euclidean) system, respectively. We place following De Donder[12] and Wiener and Vallarta[4] and using the customary tensor notation:

[10] A. Einstein, Sitz. d. preuss. Akad. d. Wiss. 1930, p. 3; also E.1.

[11] A. Einstein and W. Mayer, Sitz. d. preuss. Akad. d. Wiss., p. 110, 1930; hereafter referred to as "E-M".

[12] T. De Donder, Comptes rendus, 1928, p. 817.

$$g_{\mu\nu} = \gamma^{ab} h_{a\mu} h_{b\nu} = h_\mu{}^b h_{b\nu} \tag{2}$$

$$g^{\mu\nu} = \gamma_{ab} h^{a\mu} h^{b\nu} = h_b{}^\mu h^{b\nu}. \tag{2a}$$

In these expressions Latin indices refer to the local system, Greek indices to the Gaussian system. The quantities $h_{a\mu}$ have thus tensorial character both in the local and in the Gaussian systems, but in raising or lowering local (Latin) indices, the local tensor γ_{ab} is used, whereas in the case of Gaussian (Greek) indices, the tensor $g_{\mu\nu}$ is used. In Einstein's papers where local Cartesian coordinates are used the distinction between co- and contravariant local indices does not occur. The transformation formulas from the local to the Gaussian system now become

$$A^\nu = h_a{}^\nu A^a = h^{a\nu} A_a, \quad A_\nu = h_\nu{}^a A_a = h_{a\nu} A^a \tag{3}$$

$$A^a = h_\mu{}^a A^\mu = h^{a\mu} A_\mu, \quad A_a = h_{a\mu} A^\mu = h_a{}^\mu A_\mu \tag{4}$$

and we have, as usual,

$$h_{a\mu} h^{a\nu} = h_\mu{}^a h_a{}^\nu = \delta_\mu{}^\nu, \quad h_a{}^\mu h_\mu{}^b = h_{a\mu} h^{b\mu} = \delta_a{}^b$$

where $\delta_\nu{}^\mu$ is the Kronecker symbol. Hence

$$A^2 = A_a A^a = (h_{a\mu} A^\mu)(h_\nu{}^a A^\nu) = \gamma_{ab} h_\mu{}^b h_\nu{}^a A^\mu A^\nu = g_{\mu\nu} A^\mu A^\nu = A_\nu A^\nu$$

and the transformation formulas (3), (4), are shown to be compatible with the definition (2). Similar transformation formulas can be given for tensors of higher rank. Thus whether one works with local coordinates (Levi-Civita) or Gaussian coordinates (Einstein) is largely a matter of choice and convenience.

We now derive the generalized law of parallel displacement which formally allows local orthogonal transformations.[13] The change δ of the local components of a vector (or tensor) for an infinitesimal displacement is, in accordance with the postulate of distant parallelism,

$$\delta A_a = \delta(h_{a\alpha} A^\alpha) = \delta(h_a{}^\alpha A_\alpha) = 0 \tag{5}$$

which gives

$$h_{a\alpha} \delta A^\alpha + h^\alpha_{a.\beta} A^\alpha \delta x^\beta = 0$$

$$h_a{}^\alpha \delta A_\alpha + h^\alpha_{a.\beta} A_\alpha \delta x^\beta = 0$$

where the dot indicates covariant differentiation referred to the local coordinates, i.e. to the form $\gamma_{ab} dx^a dx^b$. From this we obtain

$$\delta A^\alpha = - A^\sigma \Gamma_{\sigma\beta}{}^\alpha \delta x^\beta \tag{6}$$

$$\delta A_\alpha = A_\sigma \Gamma_{\alpha\beta}{}^\sigma \delta x^\beta \tag{6a}$$

where

$$\Gamma_{\sigma\beta}{}^\alpha = h^{a\alpha} h_{a\sigma.\beta} = - h_{a\sigma} h^{a\alpha}{}_{.\beta} \tag{7}$$

and

$$h_{a\sigma.\beta} = h_{a\sigma,\beta} - \left\{s\beta, t\right\} h_{t\sigma} - \left\{\sigma\beta, \alpha\right\} h_{a\alpha}. \tag{7a}$$

[13] N. Rosen, "The Use of Polar Coordinates in Einstein's Geometry." S. M. Thesis, Mass. Institute of Technology; June, 1930.

As already mentioned above, the Christoffel symbols are defined through the tensor γ_{ab} by the usual formula

$$\{st, u\} = \gamma^{ub}[st, b] = \frac{1}{2}\gamma^{ub}\left(\frac{\partial \gamma_{sb}}{\partial x^t} + \frac{\partial \gamma_{tb}}{\partial x^s} - \frac{\partial \gamma_{st}}{\partial x^b}\right).$$

It is clear that a local orthogonal transformation can always be made whereby $\gamma_{ab} = \delta_{ab}$. Then obviously all the Christoffel symbols vanish and $h_{s\sigma \cdot \beta} = h_{s\sigma, \beta}$ further $\Gamma_{\mu\nu}{}^{\sigma} = h^{s\sigma} h_{s\mu, \nu}$, in accordance with Einstein's definition (E.1, p.688, Eq. (12)). $\Gamma_{\mu\nu}{}^{\sigma}$ is in general different from $\Gamma_{\nu\mu}{}^{\sigma}$ and it can be readily shown that if $\Gamma_{\mu\nu}{}^{\sigma} = \Gamma_{\nu\mu}{}^{\sigma}$ then the space whose metric is defined by the $g_{\mu\nu}$ is Euclidean.

The law of covariant affine differentiation will now be derived. Since the local components A_s of a vector are covariant relatively to a transformation of the local coordinates, $A_{s \cdot \alpha}$ is a tensor. Therefore $(h_s{}^{\sigma} A_{\sigma})_{\cdot \alpha}$ and

$$h_s{}^{\sigma}{}_{\cdot \alpha} A_{\sigma} + A_{\sigma \cdot \alpha} h_s{}^{\sigma}$$

or

$$A_{\tau \cdot \alpha} + A_{\sigma} h_s{}^{\sigma}{}_{\cdot \alpha} h_{\tau}{}^{s} = A_{\tau \cdot \alpha} - A_{\sigma} h_{s\tau \cdot \beta} h^{s\sigma} = A_{\tau \cdot \alpha} - A_{\sigma} \Gamma_{\tau\beta}{}^{\sigma} \tag{8}$$

are tensors. This tensor we shall call the covariant affine derivative of A_{τ} with respect to x^{α} and denote it by $A_{\tau;\alpha}$. Analogously for a contravariant vector

$$A^{\sigma}{}_{;\tau} = A^{\sigma}{}_{\cdot \tau} + A^{\alpha} \Gamma_{\alpha\tau}{}^{\sigma}, \tag{9}$$

which can readily be generalized to a tensor of any rank. From this we may also obtain the divergence $A^{\sigma}{}_{;\sigma}$ which is merely the contracted affine derivative.

If we take a scalar invariant Ψ and differentiate it covariantly twice we obtain

$$\psi_{;\alpha} = \psi_{\cdot \alpha} = \psi_{, \alpha}$$

$$\psi_{;\alpha;\beta} = \psi_{;\alpha \cdot \beta} - \psi_{;\sigma} \Gamma_{\alpha\beta}{}^{\sigma} = \psi_{, \alpha, \beta} - \{\alpha\beta, \sigma\}\psi_{\sigma;} - \psi_{;\beta} \Gamma_{\alpha\beta}{}^{\sigma}$$

hence interchanging α and β

$$\psi_{;\beta;\alpha} = \psi_{, \beta, \alpha} - \{\beta\alpha, \sigma\}\psi_{;\sigma} - \psi_{;\sigma} \Gamma_{\beta\alpha}{}^{\sigma}$$

and subtracting

$$\psi_{;\alpha;\beta} - \psi_{;\beta;\sigma} = \psi_{;\sigma}(\Gamma_{\alpha\beta}{}^{\sigma} - \Gamma;_{\beta\alpha}{}^{\sigma}).$$

Therefore $\Gamma_{\alpha\beta}{}^{\sigma} - \Gamma_{\beta\alpha}{}^{\sigma}$ is a tensor of the third rank, once contravariant and twice covariant. We denote it by $\Lambda_{\alpha\beta}{}^{\sigma}$. By (7) and (7a) we have

$$\Lambda_{\alpha\beta}{}^{\sigma} = h^{s\sigma}(\{s\alpha, t\} h_{t\beta} - \{s\beta, t\} h_{t\alpha} + h_{s\alpha, \beta} - h_{s\beta, \alpha}) \tag{10}$$

Einstein originally assumed that the contracted tensor $\Lambda_{\alpha\sigma}{}^{\sigma}$ plays the role of the electromagnetic potential, but has now given up this assumption (E.1, p. 691). The tensor $\Lambda_{\nu\sigma}{}^{\mu}$, however, plays a fundamental role in the unified theory.

III. The Field Equations and their Solution

Einstein sets for his field equations (E.l p. 693):

$$F^{\mu\alpha} = 0, \quad G^{\mu\alpha} = 0$$

where $F^{\mu\alpha} = \Lambda^{\nu\mu\alpha}{}_{;\nu}$ and $G^{\mu\alpha} = \Lambda^{\alpha\mu\nu}{}_{;\nu} - \Lambda^{\sigma\mu\tau}\Lambda_{\sigma\tau}{}^{\alpha}$. For the purposes of this paper it is more convenient to write them $F_{\mu\alpha} = 0$ and $G_{\alpha}{}^{\mu} = 0$. We now solve these equations under the assumption that time is not symmetrical. Wiener and Vallarta[4] have suggested that for this case the covariant quadruple has the form*

$$\begin{aligned} {}^{1}h_1 &= U, & {}^{1}h_4 &= M, & {}^{2}h_2 &= 1 \\ {}^{3}h_3 &= 1, & {}^{4}h_1 &= N, & {}^{4}h_4 &= W \end{aligned} \tag{11}$$

where U, M, N, W are functions of r only. Transformed to Cartesian coordinates the contravariant quadruple $h_s{}^{\lambda}$ becomes, as they have shown

$$\begin{aligned} &h_s{}^{\gamma} = x_s x_\gamma E(r) + \delta_{s\gamma}(s, \gamma = 1, 2, 3), \ {}_4h^{\gamma} = G(r)x_\gamma \\ &h_s{}^{4} = H(r)x_s, \ {}_4h^{4} = F(r) \end{aligned} \tag{12}$$

where $r = x_\gamma x_\gamma (\gamma = 1, 2, 3)$. This quadruple satisfies the Einstein-Mayer conditions (E-M, p. 112, Eq. (15); p. 113, Eq. (22). Since we include improper rotations their $C(r) = 0$). By a transformation of variable $x_4' = x_4 + \Psi(r)$, with Ψ arbitrary, we can always make $h_s{}^4$ vanish. Hence we may place without loss of generality $H = 0$, or $N = 0$.

The components of the tensor γ_{ab} are:

$$\gamma_{11} = 1, \quad \gamma_{22} = r^2 \sin^2\theta, \quad \gamma_{33} = r^2, \quad \gamma_{44} = 1, \quad \gamma_{ab} = 0 \quad (a \neq b) \tag{13}$$

therefore the components of the tensor $g_{\mu\nu}$ are, from (2),

$$g_{11} = U^2, \ g_{14} = g_{41} = UM, \ g_{22} = r^2 \sin^2\theta, \ g_{33} = r^2, \ g_{44} = M^2 + W^2 \tag{14}$$

and all the others vanish. Since g_{14} is not zero a change of sign of the variable t changes the sign of the term involving g_{14} in the metric fundamental form. If the variable t is to have its usual relativistic significance, time, then this can only mean that the asymmetry of past and future plays a role in the unified theory. As a matter of fact we shall see later that the condition for the existence of the electrostatic field of a particle is that there be non-symmetrical terms in time in the Riemann interval.

The tensor $\Lambda_{\nu\sigma}{}^{\mu}$ has the following non-vanishing components:

$$\begin{aligned} &\Lambda^{1}_{14} = -\Lambda^{1}_{41} = (MW' - M'W)/UW, && \Lambda^{3}_{13} = -\Lambda^{3}_{31} = (U-1)/r \\ &\Lambda^{2}_{12} = -\Lambda^{2}_{21} = (U-1)/r, && \Lambda^{3}_{34} = -\Lambda^{3}_{43} = -M/r \\ &\Lambda^{2}_{24} = -\Lambda^{2}_{42} = -M/r, && \Lambda^{4}_{14} = -\Lambda^{4}_{41} = -W'/W \end{aligned} \tag{15}$$

where the prime indicates differentiation with respect to r.[14] From these we find, after some calculation, the field equations:

* To avoid confusion we write in this and similar cases the local indices to the left of the symbols ${}^{s}h_{\lambda}$, and the Gaussian indices to the right.

$$F_{14} = -F_{41} = (1/U^2W^2)(MUWW'' - M''UW^2 - MUW'^2 - MU'WW' + M'UWW' + M'U'W^2) + 2(M - M'r)/r^2 = 0. \quad (16)$$

All the other components of the tensor $F_{\mu\nu}$ vanish identically. From the second field equation $G_\alpha{}^\mu = 0$ we find:

$$G_1{}^1 = 2(1 - U)/Ur^2 + (1/U^3W^4)(MM''UW^2 - M^2UWW'' + MUW'^2 + M^2U'WW' - MM'U'W^2 - M'^2UW^2) = 0. \quad (17)$$

$$G_1{}^4 = (1/U^2W^4)(MUWW'' - MU'WW' - MUW'^2 - M'UWW') = 0 \quad (18)$$

$$G_2{}^2 = (1/r^2U^3W^3)(2M^2U^2W - 2M^2UW - M^2U'Wr - 2M^2U^3W + 4U^2W^3 - 2UW^3 - U'W^3r - 2U^3W^3 + MM'UWr - M^2UW'r) = 0 \quad (19)$$

$$G_3{}^3 = G_2{}^2 = 0 \quad (19a)$$

$$G_4{}^1 = -[(M^2 + W^2)/U^4W^3](MUWW'' - M''UW - MU'W'^2 - MU'WW' + M'UWW' + M'U'W^2) + (2/Ur)[(M'W - MW')/UW - M/r] - (M^2+W^2)(M'W-MW')W'/U^3W^4 - M(MW'-M'W)^2/U^3W^4 = 0 \quad (20)$$

$$G_4{}^4 = (1/U^3W^4r)(M^2UWW''r + UW^3W''r - M^2UW'^2r - M^2U'WW'r - 2UW^2W'^2r - U'W^3W'r + 2U^2W'W^3 - MM'UWW'r) = 0 \quad (21)$$

and all the other components of this tensor vanish identically.

From (16) we obtain

$$\frac{d}{dr}\left(\frac{M'W - MW'}{UW} + \frac{2M}{r}\right) = 0, \quad \phi_4 = \Lambda_{4\sigma}{}^\sigma = \text{const.} = c_1 \quad (22)$$

verifying the Einstein-Mayer relation $\phi_\xi = \text{const.}$ (E.-M., p. 115, Eq. (34)).

Since at infinity space is Euclidean we have the boundary conditions: for $r \to \infty$, $M \to 0$, $M' \to 0$, $U \to 1$, $W \to 1$. Hence $c_1 = 0$ and

$$W'/W = M'/M + 2U/r. \quad (23)$$

From (18) we have

$$W'/MUW = c_2 \quad (24)$$

and substituting in (21) we obtain

$$MW'r - 2MUW - M'Wr = 0 \quad (25)$$

verifying (23). $G_\alpha{}^\mu = 0$ is therefore compatible with $F^{\mu\alpha} = 0$ provided that c_1 vanishes, independently of the boundary conditions.

Substituting (23) in (17), or in (20), gives

$$W^2 = M^2/(U - 1) \quad (26)$$

whose logarithmic derivative is $2W'/W = 2M'/M - U'/(U-1)$. Substituting W'/W from (23) we have $dU/(U-1) = -4dr/r$ whose integral is

$$U = 1/(1 + c_3{}^2/r^4) \quad (27)$$

[14] From these we readily find $\phi_1 = \Lambda_{1\sigma}{}^\sigma = 2(U-1)/r - W'/W$, $\phi_2 = 0$, $\phi_3 = 0$, $\phi_4 = (M'W - MW')/UW + 2M/r$ as in a previous paper by Wiener and Vallarta. Here $\Lambda_{\nu\sigma}{}^\mu = \Gamma_{\nu\sigma}{}^\mu - \Gamma_{\sigma\nu}{}^\mu$, whereas in the previous paper $2\Lambda_{\nu\sigma}{}^\mu = \Gamma_{\nu\sigma}{}^\mu - \Gamma_{\sigma\nu}{}^\mu$.

where c_3^2 is an integration constant. We then have from (24), (26), (27) and the boundary conditions

$$1/W = 1 + c_4 \int_r^\infty r^{-2}(1 + c_3^2/r^4)^{-3/2}dr \tag{28}$$

where $c_4 = -ic_2c_3$. From (24) or (26)

$$1/M = (1/ic_3)\left(1 + c_4 \int_r^\infty r^{-2}(1 + c_3^2/r^4)^{-3/2}dr\right)r^2(1 + c_3^2/r^4)^{1/2} \tag{29}$$

and we finally obtain the quadruple

$$
\begin{aligned}
&{}_1h^1 = 1/U = 1 + c_3^2/r^4,\ {}_2h^2 = 1,\ {}_3h^3 = 1\\
&{}_4h^1 = -M/UW = -(ic_3/r^2)(1 + c_3^2/r^4)^{1/2},\\
&{}_4h^4 = 1/W = 1 + c_4 \int_r^\infty r^{-2}(1 + c_3^2/r^4)^{-3/2}dr.
\end{aligned}
$$

All the other components vanish.

IV. Case of a Weak Field and Determination of the Integration Constants

For large values of r the quadruple h_σ^λ becomes

$${}_1h^1 = 1,\ {}_2h^2 = 1,\ {}_3h^3 = 1,\ {}_4h^1 = -ic_3/r^2,\ {}_4h^4 = 1 + c_4/r. \tag{30}$$

Einstein has suggested (E.l, p. 695) that in the first approximation the gravitational field is represented by $g_{\alpha\lambda}^* = h_{\alpha\lambda}^* + h_{\lambda\alpha}^*$, where $h_{\alpha\lambda}^*$ is an infinitesimal of the first order defined by $h_{\alpha\lambda}^* = \delta_{s\alpha}h_{s\lambda}^*$, $h_{s\alpha}^* = \delta_{s\alpha} - h_s^\alpha$. To the same approximation the electromagnetic field is defined by $a_{\alpha\mu}^* = h_{\alpha\mu}^* - h_{\mu\alpha}^*$. In the case we are considering all the components of $a_{\alpha\mu}^*$ vanish except the components a_{41}^*, a_{14}^* which give $a_{14}^* = -a_{41}^* = -ic_3/r^2$. If we now interpret this as the ordinary electromagnetic tensor then $a_{14}^* = -iE_r$. Asymptotically this should coincide with the Coulomb field for which $E_r = e/r^2$, hence the constant c_3 is to be interpreted as the electric charge. We note that this constant may be taken either positive or negative. Therefore positive and negative electricity must be taken in this theory as an empirical fact, just as in classical theory.

If we keep terms of the order $1/r$ only, all the components of the tensor $g_{\mu\nu}^*$ vanish except g_{44}^* which becomes $g_{44}^* = -2c_4/r$. To this order of approximation we may identify $g_{44}^*/2$ with the Newtonian potential as in the gravitational theory of 1916.[15] Then the integration constant c_4 is to be interpreted as the gravitational mass.

Expanding in a power series we obtain, from (27), (28), (29):

$$
\begin{aligned}
U &= 1 - e^2/r^4 + \cdots\\
1/W &= 1 + m/r + (3/10)me^2/r^5 + \cdots\\
M &= (e/r^2)(1 - m/r + m^2/r^2 + \cdots).
\end{aligned} \tag{31}
$$

[15] A. Einstein "Die Grundlage der allgemeinen Relativitätstheorie," p. 57, Leipzig, Barth, 1916.

From these expressions it is immediately seen that the electric and gravitational fields of a charged mass particle cannot be separated except when the distance r becomes sufficiently large. In the immediate neighborhood of the particle one cannot speak separately about a Coulomb field and a Newtonian field, as in classical theory, because they are inextricably bound together. This may be of importance in problems having to do with the stability of the nucleus and the constitution of the electron, but the time does not seem to have yet arrived when such problems can be treated quantitatively on the basis of the present theory, for reasons to be briefly discussed below.

V. Comparison with the Results of Einstein and Mayer

With the interpretation of the integration constants obtained in the preceding section our quadruple becomes

$$ {}_1h^1 = 1 + e^2/r^4, \ {}_2h^2 = 1, \ {}_3h^3 = 1 $$

$$ {}_4h^1 = -(ie/r^2)(1 + e^2/r^4)^{1/2}, \ {}_4h^4 = 1 + m\int_r^\infty r^{-2}(1 + e^2/r^4)^{-3/2}dr. $$

To show the identity between our results and those of Einstein and Mayer we first make the transformation $x_4 = ix'_4$, both in the local and the Gaussian variables. The only component affected is ${}_4h^1$ which becomes

$$ {}_4h^1 = (e/r^2)(1 + e^2/r^4)^{1/2}. $$

We next revert to Cartesian coordinates, obtaining the quadruple (12) with

$$ E = -(U - 1)/Ur^2, \quad F = 1/W, \quad G = -M/rUW $$

Lastly we make the transformation of the Gaussian space coordinates

$$ x'^\alpha = e^{\int (u-1)\,dr/r} x^\alpha = (1 + e^2/r^4)^{1/4} x^\alpha \ (\alpha = 1, 2, 3) $$

Remembering that $h_\sigma{}^\gamma$ transforms as a contravariant vector with respect to a change of Gaussian variables, i.e. according to the usual formula

$$ (h_\sigma{}^\gamma)' = h_\sigma{}^\sigma \frac{\partial x'^\gamma}{\partial x^\sigma} $$

we obtain the quadruple

$$ ({}_1h^1)' = ({}_2h^2)' = ({}_3h^3)' = (1 - e^2/r'^4)^{-1/2} $$

$$ ({}_1h^4)' = ex'/r'^3(1 - e^2/r'^4)^{1/4}, \ ({}_2h^4)' = ey'/r'^3(1 - e^2/r'^4)^{1/4}, $$

$$ ({}_3h^4)' = ez'/r'^3(1 - e^2/r'^4),^{4/\lambda} \ ({}_4h^4)' = 1 + m\int_{r'}^\infty r'^{-2}(1 + e^2/r'^4)^{1/4}dr. $$

where $r'^2 = x'^2 + y'^2 + z'^2$. All the other components vanish. This is precisely the solution obtained by Einstein and Mayer by a different method.

VI. The Time Symmetrical Field

By a time symmetrical field we understand one whose Riemann interval is not altered by changing $+dt$ into $-dt$. The condition for time symmetry is therefore that all the components of the tensor $g_{\mu\nu}$ shall vanish whenever either $\mu=4$ or $\nu=4$ except when $\mu=\nu=4$. This requires that $M=0$.

We solve the field equations $F^{\mu\alpha}=0$, $G_{\alpha}{}^{\mu}=0$ under this assumption. Without going into the detail of the calculations, which have already been reported at length in the preceding pages, we note the results: All the components of the tensor $F^{\mu\nu}$ vanish identically. The components of $G_{\alpha}{}^{\mu}$ which do not vanish identically are $G_1{}^1$, $G_2{}^2$, $G_3{}^3$, $G_4{}^4$. From these we get the equations:

$$G_1{}^1 = -2(U-1)/Ur^2 = 0$$

$$G_2{}^2 = G_3{}^3 = -\left[2(U-1)^2 + U'r/U\right](1/U^2r^2) = 0$$

$$G_4{}^4 = (1/U^3W^3r)(UWW''r - U'WW'r - 2UW'^2r + 2U^2WW') = 0.$$

The first equation admits evidently the only solution $U=1$, which is also a solution of the second. From the third we obtain $W''-2W'^2/W+2W'/r=0$ from which $W'r^2/W^2=\text{const}=c_1$ and $1/W=c_1/r+c_2$. Using the boundary condition $1/W=1$ for $r\to\infty$ gives $c_2=1$; hence $W=1/(c_1/r+1)=1-c_1/r$ approximately. As before c_1 may be interpreted as the gravitational mass by noting that in a weak field $g_{44}{}^*$ is twice the Newtonian potential. The quadruple is in this case:

$$_1h^1 = U^{-1} = 1,\quad _2h^2 = 1,\quad _3h^3 = 1,\quad _4h^4 = W^{-1} = (m/r+1).$$

All the other components vanish.

It is seen that in this case we obtain asymptotically the Newtonian potential just as in the previous case without time symmetry, but now there is no asymptotic electric field since all the components of $a_{\mu\nu}{}^*$ vanish. Thus the existence of an electrostatic field in the unified theory depends on the asymmetry of past and future ($-dt$ and $+dt$). We believe that this is the first instance that this asymmetry has been found to have any physical significance in connection with a field theory. The existence of the gravitational field, on the other hand, is apparently not connected with this asymmetry. We may perhaps have found here the fundamental difference, superficial similarity notwithstanding, between the gravitational and the electric field of a charged mass particle.

VII. Concluding Remarks

In the absence of a law of motion, not yet discovered, the path of an exploring particle in the unified field cannot be calculated. If it were assumed, for instance, that the orbit of a mass particle in a pure gravitational field is a geodesic with respect to the Riemannian ds^2, as in the 1916 theory, then a simple calculation shows that in the case of Mercury the advance of the perihelion would be $7''$ per century, approximately. For the same reason the path of a light ray in the solar field cannot be predicted. If it were assumed that the path is a geodesic of zero length with respect to the Rieman-

nian interval, as in the 1916 theory, then the present experimental evidence would likewise furnish proof against rather than for the unified theory.

The shift of spectral lines towards the red, on the other hand, does not depend on the law of motion of an exploring particle, but only on the component g_{44} of the Riemann metric. One sees immediately from (14) and (31) that the red shift obtained on the basis of the present theory is the same to a first approximation as that predicted on the basis of the 1916 theory. To higher orders of approximation the present theory would lead to expect an effect depending also on the electric charge, but it seems difficult to devise an experiment to test this conclusion. In addition to the first order effect just discussed, the only evidence in favor of the unified theory seems to be that asymptotically it yields the classical Coulomb field and the classical Newtonian potential.

The two burning questions connected with the unified theory are, first, the discovery of the law of motion and, second, the discovery of a connecting link with quantum theory. The solution of these problems will inevitably lead to crucial experimental tests of its physical significance. While still far from the goal of investigations which we have pursued for some time, a few remarks may properly find expression at this time.

Because of the non-linear character of the field equations it is to be expected, just as in the case of the 1916 theory of gravitation, that these equations and the law of motion are not independent. If this conjecture is correct, then a systematic investigation by the method of Lanczos must lead either to the law of motion or to the proof that there is none. It should be emphasized that the choice of a law of motion is a considerably more difficult matter in the present theory than in the 1916 theory, because in the latter case the Riemannian geodesic is the natural generalization of the Euclidean straight line, so that even without a systematic investigation one would expect on the basis of the Principle of Equivalence that the path of the exploring particle is a geodesic. Such is not the case in the unified theory because there are too many intrinsically defined lines in the Einstein geometry, not merely the Riemannian geodesics, which asymptotically reduce to Euclidean straight lines. Hence the difficulty of finding the law of motion without a systematic investigation.

Until recently there seemed to be little doubt that the connecting link between the unified theory and quantum theory would be found through some generalization of the Dirac equations, as suggested by Wigner, Wiener and Vallarta, Tamm, Fock, Weyl and others. None of these attempts has proved satisfactory and some of them have been shown to be definitely erroneous. An entirely new method of attack, however, has been opened by the quantum electrodynamics of Heisenberg, Pauli, Jordan, and Fermi, but even then no great progress seems possible before this theory has been divested of its extreme formalism. A further discussion of these questions would evidently be very much out of place here, but we hope to return to them in the not too distant future.

THE GIBBS-DALTON LAW OF PARTIAL PRESSURES

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Abstract

Various formulations of Dalton's law are investigated thermodynamically. The Gibbs formulation is shown equivalent to the statement: The concentration of a gas is the same at equilibrium on either side of a membrane permeable to it alone. The ordinary form of Dalton's law has only a limited equivalence with the Gibbs form. The Lewis and Randall rule of fugacity is shown in many ways analogous to the Gibbs-Dalton law. Application to experimental data shows that the Gibbs-Dalton law, like the Lewis and Randall rule, though possible for gases which do not follow Boyle's law, is only an approximation. In the cases examined, the errors are opposite in sign to those of the Lewis and Randall rule. An outline is given for the application of the Gibbs-Dalton law to the study of equilibrium in gases, and the useful field of application is indicated.

1. Thermodynamic Theory

GIBBS formulated Dalton's law as follows:[1] "The pressure in a mixture of different gases is equal to the sum of the pressures of the different gases as existing each by itself at the same temperature and with the same value of its potential." He states "It is in this sense that we should understand the law of Dalton, that every gas is as a vacuum to every other gas." A study of Dalton's paper[2] shows that the spirit of Dalton's principle is very closely represented in the Gibbs formulation, which will hereinafter be called the Gibbs-Dalton law.

The Gibbs-Dalton law is in sharp contrast to the formulations now commonly given, which either omit entirely the essential idea of equilibrium,[3] implied in the phrase "at the same temperature and with the same value of its potential," or state[4] laws of vapor pressure of liquids in contact with inert gases, which laws assume zero the effects of varying pressure and composition, equations for which were given by Poynting and Raoult.

Gibbs disentangled the essential principle from these latter effects and generalized it, ignoring the unimportant distinction between vapor and gas.

* Contribution No. 242.

[1] Gibbs, Scientific Papers. I. Thermodynamics, p. 155. Longmans, Green and Co., New York, 1906 and 1928.

[2] Dalton, Nicholson's Journ. Science 5, 241 (1801).

[3] Thus the equivalent of proposition (2) below is given by the Encyclopedia Britannica, Ed. 14, 6, 995; 13, 389 (1929), by Schaefer, Einführung in die theoretische Physik, II, 92, Berlin and Leipzig, 1929, and in a large number of texts on physical chemistry. No text has been found which shows an influence of Gibbs' formulation.

[4] As in elementary texts on physics, following Ganot, Traité de Physique, Ganot, Paris. 1872.

He derived as a consequence of his formulation a series of propositions and pointed out that they, as well as the original formulation, are consistent and possible for gases obeying when pure any equations of state whatever. These propositions are involved in one extraordinarily condensed statement (page 157, just below equation 283). They may be stated as follows.[5] 1. The concentration[6] of any gas in a mixture is the same at equilibrium on either side of a membrane permeable to it alone. 2. The pressure of a gaseous mixture is equal to the sum of the individual gases as existing each by itself with the same temperature and volume as the mixture. (This is the common form of Dalton's law.) 3. Each of the quantities: the total energy, heat content, entropy, and $p-T$ and $v-T$ thermodynamic potentials (or free energies) equals the sum of the respective values for the individual gases as existing each by itself with the temperature and volume of the mixture. To these may be added another consequence, 4: The heat capacity at constant volume of a mixture of gases equals the sum of the heat capacities of the individual gases as existing each by itself at the temperature and volume of the mixture.

For let U be the energy and C the constant-volume heat capacity of the mixture, and U_{iv} and C_{iv} be the energy and heat capacity of any gas (i) of the mixture but in the pure state at the temperature T and the volume V of the mixture.[7] Then Gibbs shows that $U=\Sigma_i U_{iv}$, from which $(\partial u/\partial T)_v = \Sigma_i(\partial u_{iv}/\partial T)_v$. Since $(\partial u/\partial T)_v = C$ we have therefore that $C=\Sigma_i C_{iv}$.

Gibbs states only one proposition in the nature of a converse, namely: 5. If the total $v-T$ thermodynamic potential (or Helmholtz free energy) of the mixture is equal to the sum of the values of this function for the several component gases existing each by itself in the same quantity as in the gas mixture and with its temperature and volume, then the Gibbs-Dalton law and all its consequences must hold. Two other converse propositions (6 and 7) may be added.

6. If the concentration of each gas in a mixture is the same at equilibrium on either side of a membrane permeable to it alone, the Gibbs-Dalton law and its consequences must hold. Let n_1 be the number of moles (or grams) of gas 1 in the mixture, of which the volume is V, and the pressure p, and let n_{1e}, V_{1e}, and p_{1e} be the corresponding quantities for the pure gas 1 in such a state as to be in equilibrium with the mixture with respect to transfer of gas 1. p_{1e} will be hereafter called the equilibrium pressure, and n_{1e}/V_{1e} the equilibrium concentration. Then by hypothesis,

$$n_1/V = n_{1e}/V_{1e}. \tag{1}$$

Gibbs' equation 98 is

$$dp = (S/V)dT + (n_1/V)d\mu_1 + (n_2/V)d\mu_2 + \text{etc.} \tag{2}$$

[5] With less elegance, and with some redundancy.

[6] As in moles per liter, or grams per cc. Dalton uses "density, considered abstractly," and Gibbs, "separate density," or simply "density," for what is now called concentration.

[7] Naturally also, the same mass of pure gas is considered as is present in the mixture. This is understood to be the case in any of the comparisons, as otherwise no comparison is possible.

By substitution,

$$dp = (S/V)dT + (n_{1e}/V_{1e})d\mu_1 + (n_{2e}/V_{2e})d\mu_2 + \text{etc.} \tag{3}$$

Applying equation 98 in succession to the pure gases 1, 2, etc., we have

$$n_{1e}/V_{1e} = (\partial p_{1e}/\partial \mu_1)_T,\ n_{2e}/V_{2e} = (\partial p_{2e}/\partial \mu_2)_T, \text{ etc.} \tag{4}$$

By substitution we have at constant temperature

$$dp = (\partial p_{1e}/\partial \mu_1)_T\, d\mu_1 + (\partial p_{2e}/\partial \mu_2)_T\, d\mu_2 + \text{etc.} \tag{5}$$

Since each pure gas remains in equilibrium with the mixture, μ and $d\mu$ for any gas is the same in the mixture as for the pure gas. Therefore the last equation may be immediately integrated at constant temperature to

$$p = p_{1e} + p_{2e} + p_{3e} + \text{etc.} + f(T), \tag{6}$$

since each term like $(\partial p_{1e}/\partial \mu_1)_T d\mu_1$ is at constant temperature of the form $(dz/dx)dx$, the variables having been separated. But $f(T)$ must be zero, in order that the expression shall reduce to the identity $p = p_{1e}$ for the special case in which the mixture is replaced with pure gas 1. Evidently the following law is in all ways equivalent to the Gibbs-Dalton law; (1): The concentration of each gas in a mixture is the same at equilibrium on either side of a membrane permeable to it alone.[8]

It should be noted that proposition 2, which is the form of Dalton's law commonly taught in texts on physical chemistry, is a consequence of the Gibbs form, but is less inclusive, as it asserts nothing about equilibrium. We may now show, however, that: (7). If we assume that the Gibbs form is true in the limiting case of infinitely large volumes, then proposition 3 asserted for all pressures, requires the validity of the Gibbs form at all pressures. Let the pure gases be kept throughout the variations at the volume and temperature and in the quantities present in the mixture, and consider variations of V and of n_1, n_2, etc. Let the pressure and potential of the pure gas 1 at the temperature and volume of the mixture be represented by p_{1v} and μ_{1v} and likewise for other species. Then proposition 2 may be written

$$p = \Sigma(p_{1v} + p_{2v} + \text{etc.}) \tag{7}$$

Then

$$(\partial p/\partial n_1)_{Tvn} = (\partial/\partial n_1)_{Tvn}\Sigma(p_{1v}) = (\partial p_{1v}/\partial n_1)_{Tv}. \tag{8}$$

But[9]

$$(\partial \mu_1/\partial V)_{Tn} = -(\partial p/\partial n_1)_{Tvn} \text{ and } (\partial \mu_{1v}/\partial V)_{Tn_1} = -(\partial p_{1v}/\partial n_1)_{Tv} \tag{9}$$

[8] The same is true of the proposition: (1a) There is equilibrium when the concentration of a gas is the same on either side of the semipermeable membrane, (the temperature being uniform). This is because Gibbs proves (reference 1, page 67) that equality of potentials and temperature is necessary *and sufficient* for equilibrium. But even without this, physical reasoning shows that there is no point in observing the logical distinction between (1) and (1a).

[9] These equations result from cross differentiation of Gibbs' Eq. (88).

and therefore

$$(\partial\mu_1/\partial V)_{Tn} = (\partial\mu_{1e}/\partial V)_{Tn_1}. \tag{10}$$

Hence, since equilibrium is supposed at zero pressure when in equal volumes the numbers of moles of kind 1 are equal in the pure gas and in the mixture, these volumes may be equally reduced as much as we please without changing the numbers of moles; the potentials will change by the same amounts for the pure gas and the mixture, so that their differences will remain zero, and the system will remain in equilibrium. Hence $p_1 = p_{1e}$, and similarly $p_2 = p_{2e}$, etc., and therefore

$$p = \Sigma(p_{1e} + p_{2e} + \text{etc.}) \tag{11}$$

But we believe that the Gibbs-Dalton law holds at zero pressure. When therefore we are interested solely in testing hypothesis or law by means of data, and not at all in developing or presenting a logical system, we may regard the simple additivity of pressures, as expressed in the common form of Dalton's law (proposition 2) as equivalent to the Gibbs formulation.

The theoretical treatment is incomplete if we omit to consider the form in which Dalton's law has frequently been used by specialists interpreting data. This is; (8) the equilibrium pressure of any gas in a mixture equals the total pressure of the mixture times its mole fraction in the mixture, or

$$p_{ie} = p(n_i/\Sigma_i n_i) = px_i, \tag{12}$$

where n_i is necessarily in moles rather than grams, and x_i is the mole fraction. When we come to examine the applicability of the Gibbs-Dalton law we should compare any success obtained with that obtained by the use of this form, which will be called Dalton's law in the ideal gas form.

Lurie and Gillespie[10] pointed out that this form of Dalton's law contains the laws of Boyle and Avogadro. As their proof was incomplete in form, a complete proof is herewith given. Granted that $p_{ie} = px_i$ for every gas in a gas mixture. Then obviously $p = \Sigma_i px_i = \Sigma_i p_{ie}$, from which, according to the proof given by Gibbs, the concentration of any gas in the mixture, as n_i/V, equals the concentration of the pure gas when under its equilibrium pressure, as n_{ie}/V_{ie}. We have then

$$p_{1e} = px_1 = pn_1/\Sigma_i n_i \tag{13}$$

and

$$V_{1e}/n_{1e} = V/n_1 \tag{14}$$

From which,

$$p_{1e}V_{1e}/n_{1e} = pV/\Sigma_i n_i \tag{15}$$

Similarly

$$p_{2e}V_{2e}/n_{2e} = pV/\Sigma_i n_i \tag{16}$$

[10] Lurie and Gillespie, Journ. Amer. Chem. Soc. **49**, 1146 (1927).

Hence

$$p_{1e}V_{1e}/n_{1e} = p_{2e}V_{2e}/n_{2e}. \tag{17}$$

These equations must hold for equilibrium variations of the variables. Among the variables T, p, μ_1, μ_2, $\cdots$, etc., only one relation (the fundamental equation) exists. Hence a variation in μ_1 is possible at constant μ_2, μ_3, etc., and T. Therefore at constant temperature a variation of p_{1e} is possible at constant p_{2e}, and constancy of p_{2e} requires at constant temperature a constant concentration n_{2e}/V_{2e}. Hence $p_{1e}V_{1e}/n_{1e}$ is a constant during variations of p_{1e} and if n_{1e} is arbitrarily held constant, pV is constant. This is Boyle's law. Furthermore, the constant $p_{1e}\ V_{1e}/n_{1e}$ is evidently independent in magnitude of the character of gas 1, and would be the same for some other gas. Hence this equation includes Avogadro's law, that n is the same for any gas when p and V are the same. If, also, these relations hold at any constant temperature, the expansions of the different gases must be alike. Hence this form of Dalton's law contains all of the laws of ideal gases except those relating to the energy (such as $(\partial u/\partial V)_T = 0$, or that pV is proportional to *thermodynamic* temperature), and, in the lack of a conventional name, may well be called Dalton's law in the ideal gas form.

The rule of Amagat,[11] that the volume of a gaseous mixture equals the sum of the volumes of the individual gases as existing each by itself at the temperature and (total) pressure of the mixture, is not here regarded as a form of Dalton's law.[12] It is analogous to the law of additive pressures (proposition 2) in many ways. Thus the fugacity rule of Lewis and Randall[13] bears to this rule a relation similar to that existing between the Gibbs-Dalton law and the additivity of pressures. This fugacity rule, when the variable is changed from fugacity to chemical potential, states that the difference between the chemical potential of a gas in equilibrium with a mixture and the potential it would have at the temperature and pressure of the mixture is the same as for a system of ideal gases, i.e., $RT \ln x$. According to the Gibbs-Dalton law the difference between the potential of a gas in equilibrium with a mixture and the potential it would have at the temperature and volume of the mixture is the same as for a system of ideal gases, i.e., zero. As stated by Lewis and Randall, their rule implies the additivity (at constant temperature and pressure) of volume and heat content. As shown by the author,[14] the additivity of volumes is enough, together with suitable assumptions relating to the gases at zero pressure (which may be, for example, that the rule is exact at zero pressure) to establish the rule. Furthermore, the rule makes the partial molal volume $\overline{V}_1$ of a gas in a mixture equal to the molal volume V_{1p} of the pure gas at the temperature and

[11] Amagat, Ann. chim. phys. [5] **19**, 384 (1880); Compt. rend. **127**, 88 (1898).

[12] Fortunately very few authors have called it Dalton's law. Curiously, this form was actually stated by Dalton, whereas the common form was not stated by him, though it was used. The two forms are naturally equivalent when ideal gases are under consideration, as was the case in all of Dalton's considerations.

[13] Lewis and Randall, Thermodynamics, McGraw-Hill Book Co. Inc., New York, 1923.

[14] Gillespie, Journ. Amer. Chem. Soc. **47**, 305 (1925).

pressure of the mixture; that is, $\overline{V}_1 - V_{1p}$ and its temperature and pressure derivatives become zero. Examination now of equations 6a, 7, 10, and 14 of a previous paper[15] will show that this leads to the following consequences. The difference between any one of the functions: the total energy, heat content, entropy, and $p-T$ and $v-T$ thermodynamic potentials for the mixture, as against the sum of the corresponding values of any function for the individual gases taken at the temperature and pressure of the mixture, must have at all pressures the same value as at zero pressure. This difference is zero for the energy and heat content, but is expressed in terms involving log x in the case of the entropy and the two thermodynamic potentials, whereas according to the Gibbs-Dalton law the corresponding differences (taken at the temperature and volume of the mixture) are all zero. Finally, the rule makes the heat capacities at constant pressure additive, since these are the temperature derivatives at constant pressure of the additive heat contents.

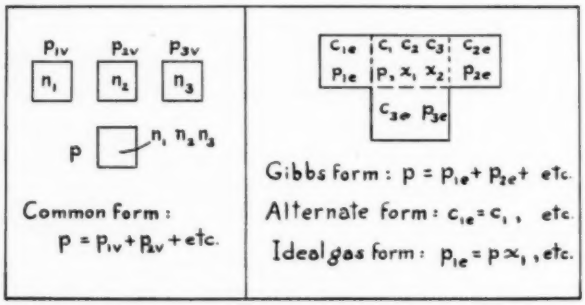
p_{1v} p_{2v} p_{3v}
n_1 n_2 n_3
p
n_1 n_2 n_3
Common form:
$p = p_{1v} + p_{2v} + \text{etc.}$
c_{1e} c_1 c_2 c_3 c_{2e}
p_{1e} p x_1 x_2 p_{2e}
c_{3e} p_{3e}
Gibbs form: $p = p_{1e} + p_{2e} + \text{etc.}$
Alternate form: $c_{1e} = c_1$, etc.
Ideal gas form: $p_{1e} = p x_1$, etc.

Fig. 1. Illustrating various forms of Dalton's law.

In Fig. 1 some of the principal relations among the forms of Dalton's law are shown and the use of symbols illustrated.

2. Comparison of the Gibbs-Dalton Law with Data

Figure 2 (L−G) Data of Lurie and Gillespie. These data are the values of p and x_1 for mixtures of ammonia (subscript 1) and nitrogen (subscript 2) at 45° observed for corresponding values of p_{1e}, which is the vapor pressure of barium chloride octammine corrected for the total pressure. In the former comparison, the quantities calculated and observed were the equilibrium pressure p_{1e}. A more direct comparison is here given between the calculated and observed values of x_1. In the present calculations from the Gibbs-Dalton law the Beattie-Bridgeman equations of state[16] for both gases were used. Fig. 2 shows the observed minus the calculated mole percent ammonia in percent deviation of the observed value. The percentage deviations are shown for the Gibbs-Dalton law (circles, solid line) and for Dalton's law in the ideal gas form (squares, broken line).

[15] Gillespie, Phys. Rev. **34**, 1605 (1929).
[16] Beattie and Bridgeman, Proc. Amer. Acad. Arts and Sci. **63**, 229 (1928).

Figures 2 and 3. Data of Larson and Black.[17] These are the values of p and x_1 for mixtures of ammonia (subscript 1) and hydrogen-nitrogen (subscript 2) in a constant mole ratio of 3:1, observed for corresponding

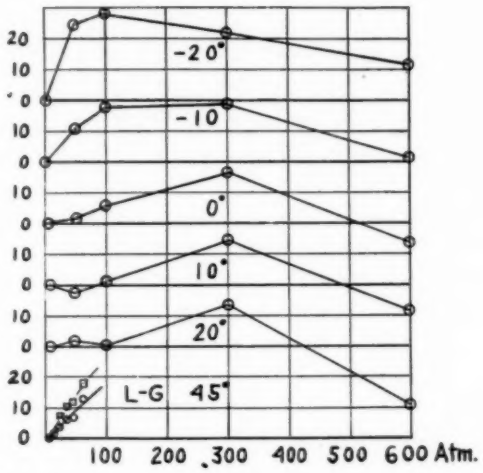

Fig. 2. Errors of the Gibbs-Dalton law.

values of p_{1e}, the vapor pressure of liquid ammonia corrected for the lowering due to dissolved gas and the raising due to the increased total pressure. The temperatures are from $-20°$ to 20°C. The thermodynamic calculations

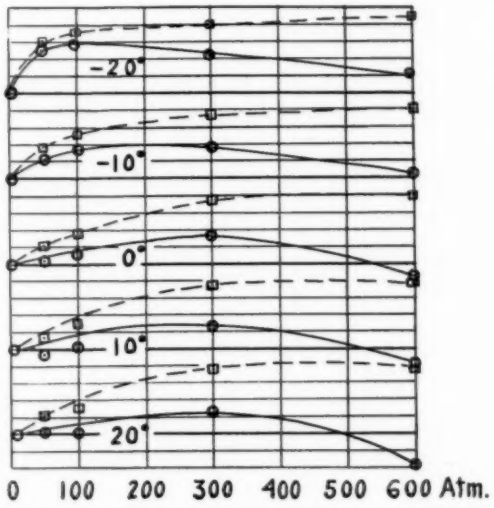

Fig. 3. Errors of the Gibbs-Dalton law.

were performed by Cupples[18] for the purpose of determining the existence of a true "solvent action." Previous authors had ascribed deviations from

[17] Larson and Black, Journ. Amer. Chem. Soc. **47**, 1015 (1925).

Dalton's law in the ideal gas form to the existence of a solvent action. The solvent action, as defined by him, is zero when the concentration of gas is the same at equilibrium on either side of an appropriate membrane. From the theoretical part above, it is evident that such calculations afford a direct test of the Gibbs-Dalton law. These calculations extend to 600 atmospheres, at which point the vapor pressure has been corrected to double its original value for the increase in total pressure. In applying this correction, the equation of state of ammonia has to be extrapolated well into the region of supersaturation and it is difficult or impossible at present to determine just how much reliance may be put on the calculations at the higher pressures. Consequently, more emphasis will here be put on the trends at the lower pressures. Figure 2 shows the percentage deviation, observed minus calculated mole percent ammonia, the percentage being based on the observed. As in the previous figure the deviation must be zero when the total pressure is equal to the normal vapor pressure, the mole fraction of ammonia then being unity. In Fig. 2 the points are connected by straight lines in order not to prejudice the smoothing. In Fig. 3 smoothed curves are drawn (solid lines near the circles) for the Gibbs-Dalton law, and also for the ideal gas form (broken lines and squares). The lines of zero deviation are heavy, and the scale divisions of ordinates are 10 percent in all cases.

Examination of the figures shows that the Gibbs-Dalton law fails to fit the data, especially at the lower pressures, where the calculations are most certain. It is true that in Fig. 2 at 10 and 20° the deviations are substantially zero for 50 and 100 atmospheres, and if only these two isotherms were given, one might conclude that the deviations appear to be zero, perhaps even above 300 atmospheres. This would involve the ignoring of the 300 atmosphere points. Taking the picture as a whole there appears to be no doubt that it is rather the 50 and 100 atmosphere points which are in error, and that the family of curves should be drawn with maxima, which move towards higher pressure at higher temperature. The deviations of the Gibbs-Dalton law are in all cases smaller than those of the ideal gas form, but the difference is not in most cases impressive. There is a hint that the contrary may be the case at sufficiently high pressures.

The existence of maxima in the curves seems consistent with the findings of Masson and Dolley[19] in the cases of mixtures of ethylene with oxygen; here the deviations from the law of additive pressures also increase at first with pressure and pass through a maximum, in some cases changing sign at the highest pressures. In general it appears that the maximum occurs at lower pressures, the less perfect the gas mixture.

The foregoing conclusions, as respects the data of Larson and Black, are not the same as those drawn by Cupples. The principal reason for this appears to be that his plot, based on different variables, does not show the zero deviations which must occur at all temperatures in the limiting case in which the gas phase is pure ammonia.

[18] Cupples, Journ. Amer. Chem. Soc. **51**, 1026 (1929).

[19] Masson and Dolley, Proc. Roy. Soc. London **103A**, 524 (1923).

3. Application

By virtue of certain assumptions as to the properties of gaseous mixtures and pure gases at infinitely low pressures, which may for present purposes be freely expressed as follows: the behavior of real gases approaches that of ideal gases at zero pressure,—it is possible to correlate equilibrium data in a purely thermodynamic manner with pressure data for the pure gases in question and for mixtures of them, together with specific heats also, if temperature correlation is included. To avoid the necessity of data on gas mixtures, some assumption may be made regarding the pressures or volumes of gaseous mixtures, compared with those of their constituent pure gases. Only three such assumptions are to be found as the basis of methods which have received any degree of attention.[20] They are (1) the additivity of pressures or the Gibbs-Dalton law, (2) the additivity of volumes or the Lewis and Randall rule of fugacity, and (3) the additivity of equation of state constants, usually described in publications from this laboratory as linear combination of constants.[21]

Examination of the pressure data of mixtures, as well as application to equilibria, has shown that the third method is in general more accurate than the other two methods.[22] Nevertheless the former two may be of service in special instances, due to the fact that in certain types of calculation they will require much less computation than the third method.

For calculations of the effect of pressure upon equilibrium constants the Lewis and Randall rule is especially adapted. It fits the Haber equilibrium data up to about 100 atmospheres.[23] A mass action equation may readily be derived from the Gibbs-Dalton law and the individual equations of state, but it has the disadvantage that the expression for the effect of pressure on the equilibrium constant involves terms in mole fractions, which would greatly complicate the calculation. Neither method can be trusted to give accurately the effect of varying mole fraction on the equilibrium constant.

For the calculation of the concentrations of a gaseous mixture which is in equilibrium with a liquid or other phase, or even for the calculation of the mole fractions of such a mixture, the Gibbs-Dalton law is especially adapted. It has an important advantage over the Lewis and Randall rule, that the

[20] We omit here the usual Dalton law in the ideal gas form, as its use is inconsistent with any equation of state but that of Boyle.

[21] *I. e.*, linear in all the constants which are of the first power in the volume and in the square root of the cohesive pressure A constant, which root is of the first power.

[22] Evidence in support of it may be marshalled from the following papers. Lurie and Gillespie reference 10; Keyes and Burks, Journ. Amer. Chem. Soc. **50**, 1100 (1928); Beattie, Journ. Amer. Chem. Soc. **51**, 19 (1929); Gillespie, Phys. Rev. **34**, 352 (1929); Beattie and Ikehara, "An Equation of State for Gas Mixtures. II. A Study of the Methods of Combination of the Constants of the Beattie-Bridgeman Equation of State." (to be published soon); and Gillespie and Beattie, "Correlation of the Haber Equilibrium Data with Compressibilities and Specific Heats of the Pure Gases by Means of a Rational Mass Action Equation" (to be published soon).

[23] Gillespie, Journ. Amer. Chem. Soc. **48**, 28 (1926).

equations of state do not need such severe extrapolation into the region of supersaturation. Thus for the data of Lurie and Gillespie at a total pressure of 60 atmospheres, the equation of state needs extrapolation from 7.1 to 60 atmospheres in the one case and from 7.1 to but about 7.4 atmospheres in the other.

An outline of the calculations from the Gibbs-Dalton law follows.

Let $p_1=f_1\ (T,\ n_1/V)$, $p_2=f_2\ (T,\ n_2/V)$, etc., be the equations of state of the several gases. Then $p=f_1\ (T,\ n_1/V)+f_2\ (T,\ n_2/V)+$etc., where p and V are the pressure and volume of the mixture and n_1, n_2, etc., are the numbers of moles in the mixture.

Solution for the equilibrium pressure, p_{1e}, of a gas (1) in the mixture from known values of p and the mole fractions x_1, x_2, etc., proceeds by putting $\Sigma_i n_i=1$ and finding by trial a value of V which will satisfy

$$p = f_1(T,\ x_1/V) + f_2(T,\ x_2/V) + \text{etc.} \tag{18}$$

When the computed pressure finally checks the observed pressure, the final values of $f_1\ (T,\ x_1/V)$, $f_2\ (T,\ x_2/V)$, etc., are the calculated equilibrium pressures. Any equilibrium pressure is the pressure of the pure gas that would be in equilibrium with the mixture; and, when a liquid is in equilibrium with the mixture, the equilibrium pressure is equal to the vapor pressure of the liquid, corrected by means of Poynting's equation for the increased total pressure, and by means of Raoult's law for the solubility of the inert gases in the liquid.[24]

Solution for the mole fractions from known equilibrium pressures and the known pressure of the mixture proceeds as follows. Calculate n_1/V from the equilibrium pressure p_{1e} of gas 1 by means of the equation of state:

$$p_{1e} = f_1(T,\ n_1/V) \tag{19}$$

by successive approximations. If the mixture is binary, $p_{2e}=p-p_{1e}$, and n_2/V may be similarly calculated from the equation of state of gas 2. If the mixture is binary with respect to a gas (1) like ammonia and a mixture (2) of gases in constant mole ratio, such as a 3:1 hydrogen-nitrogen mixture, treat this constant mixture (which will not change greatly through differential solubility) as a pure gas whose constants are obtained by "linear combination of constants,"[21,22] unless the equation for the mixture has already been determined. If the mixture is ternary or more complicated, another equilibrium pressure must obviously be known for each added constituent. When in any case the values of n_1/V, n_2/V, etc. have been calculated, any mole fraction is immediately found from the relation

$$x_i = \frac{n_i/V}{\Sigma_i(n_i/V)}. \tag{20}$$

In order to avoid some of the successive approximations, the volume equation of Beattie[25] may be used. The calculations may also be done

[24] This latter correction was found small by Larson and Black (17).

[25] $(V/n_1)=f_1\ (T,\ p)$, Beattie, Proc. Nat. Acad. Sci. **16**, 14 (1930).

throughout by means of graphs. It is of course unnecessary to introduce fugacities[26] unless some of the experimental information is found expressed in terms of them.

4. The Sign of the Errors in the Application

At low pressures the partial volume $\overline{V}_1$ of a gas in a mixture is found in general to be greater than the molal volume V_{1p} of the pure gas at the pressure and temperature of the mixture.[27] From an equation previously given[23]

$$RT \ln f_1 = \int_0^p (\overline{V}_1 - RT/p)dp + RT \ln px_1 \qquad (21)$$

the signs of the errors to be expected of the Lewis and Randall rule at low pressures can readily be determined. For according to the rule, $\overline{V}_1 = V_{1p}$, hence in applying the rule a value of the integral is virtually used which is too small algebraically. Hence the mole fraction x_1 calculated by the rule from a known fugacity f_1 (determined from the vapor pressure, of which it is an increasing function) will come out too large.

In the case of the Gibbs-Dalton law, no special study has been made of the analogous quantity $(\partial p/\partial n_1)$. It is worthy of notice, however, that the mole fractions calculated from the vapor pressures are too low at the lower pressures in the cases examined above. Thus, at least in these cases, the true value evidently lies between those given by the two approximate methods.

[26] If this is desired, the paper of Cupples may be consulted. (18).
[27] Gillespie, Phys. Rev. **34**, 352 (1929).

A RATIONAL BASIS FOR THE THERMODYNAMIC TREATMENT OF REAL GASES AND MIXTURES OF REAL GASES

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Abstract

From the general laws of thermodynamics and two isothermal assumptions, one of which states that at constant temperature the energy of a pure gas approaches a function of the temperature in the following manner:

$$U_1 = f_1(T) + \zeta_1 p$$

and the other that at constant temperature and composition the ratio of the equilibrium pressure of a gas in a mixture to the product of the mole fraction of the gas in the mixture multiplied by the total pressure of the mixture approaches unity in the following manner:

$$\frac{p_{ei}}{px_i} = 1 + \xi_i p$$

where ζ_1 and ξ_i are bounded parameters, it has been shown that the following relations hold for real gases or mixtures of real gases at infinitely low pressures:

(a). The ratio of the equilibrium pressure of a gas to the product of its mole fraction in the mixture multiplied by the total pressure of the mixture is unity.

(b). The ratio of the equilibrium concentration of a gas to its concentration in the mixture is unity.

(c). The ratio of the sum of the equilibrium pressures (or equilibrium concentrations) of the component gases to the total pressure (or concentration) of the gas mixture is unity.

(d). The entropy, energy, heat content, thermodynamic potentials and heat capacities at constant volume and at constant pressure of a mixture of gases are equal respectively to the sums of the entropies, energies, heat contents, thermodynamic potentials and heat capacities of the component gases existing each by itself with the same value of its volume, temperature and chemical potential as in the mixture. The above statement holds when the component gases exist each by itself with the same value of its volume and temperature as in the gas mixture and with the ratio of its concentration to its concentration in the gas mixture equal to unity.

(e). The energy, heat content and heat capacities of pure gases and of gas mixtures of constant composition are functions of the temperature.

(f). The difference between the heat capacity at constant pressure and that at constant volume of a pure gas or of a gas mixture is equal to the product of the total number of moles present multiplied by the gas constant R.

(g). The pressure-volume product for a pure gas or for a gas mixture is equal to the product of the total number of moles present multiplied by RT where R is a universal constant and T the Kelvin temperature.

* Communication No. 240.

1. Introduction

IN ORDER to give a general thermodynamic treatment for mixtures of real gases comparable to that given by Gibbs[1] for mixtures of ideal gases it is necessary to make several assumptions. Gillespie[2] has shown that a general relation for the isothermal variation of the mass action function K_p (which represents chemical equilibria in gaseous systems) can be derived from general thermodynamic considerations together with the one assumption: At very low pressures the "equilibrium pressure" of each gas in a mixture is equal to the product of the mole fraction of that gas in the mixture multiplied by the total pressure of the mixture. It has also been shown[3] that relations for the variation of the thermodynamic properties of gas mixtures with temperature and pressure (or volume) can be derived from the above assumption and one other: At very low pressures the energy of a mixture of gases is equal to the sum of the energies of the component gases existing each by itself at the temperature and in the total volume of the mixture. Besides these two assumptions for gas mixtures, there was used the assumption that at very low pressures the pressure of a pure gas is equal to nRT/V.

De Donder[4] has given relations for some of the thermodynamic properties of gas mixtures on the assumption that, as the pressure on the mixture is decreased at constant temperature, certain properties of the gas mixture approach those of mixtures of ideal gases. Keyes[5] has given an equation for the mass action function K_p by use of the kinetic considerations from which the Keyes[6] equation of state was derived.

It is to be noted that the assumptions which it has been found necessary to make relate to the thermodynamic properties of gaseous systems under low pressures. In the following treatment it is shown that all of the necessary relations for the treatment of real gases and mixtures of real gases can be derived from two assumptions, each of which are for isothermal conditions.

We shall consider two pressure regions:

(1) *Low pressures*, at which for all practical purposes terms of the order of p^2 can be neglected in comparison with unity, or with terms of the order of p.

(2) *Very low pressures*, at which for all practical purposes terms of the order of p can be neglected in comparison with unity. An asterisk placed after a thermodynamic quantity is used to denote the values which the quantity in question assumes in the region of very low pressures.

From an experimental standpoint one atmosphere may be considered a "low pressure" for the permanent gases at room temperature; and one centimeter of mercury, a "very low pressure."

[1] Gibbs, The Scientific Papers of J. Willard Gibbs, Longmans, Green and Co., New York, 1906; Vol. I, p. 150.

[2] Gillespie, Jour. Amer. Chem. Soc. **47**, 305 (1925); ibid. **48**, 28 (1926).

[3] Beattie, Phys. Rev. **31**, 680 (1928); ibid. **32**, 691, 699 (1928).

[4] De Donder, Compt. rend. Acad. Sci. Paris **180**, 1922 (1925). "L'Affinité," Gauthier-Villars, Paris, 1927.

[5] Keyes, Jour. Amer. Chem. Soc. **49**, 1393 (1927).

[6] Keyes, Amer. Soc. Refrig. Eng. Jour. **1**, 9 (1914); Proc. Nat. Acad. Sci. **3**, 323 (1917).

Throughout the present treatment we shall use the greek letters α, β, ζ, η, κ and ξ to denote bounded parameters; that is, parameters whose numerical magnitudes do not exceed an assignable upper limit. When occurring with the subscript 1, they refer to pure gases without reference to any gas mixture, and vary with the temperature; when used without subscripts or with the subscript i they refer to a mixture of gases and vary with the temperature and the composition of the mixture.

2. The System Under Consideration

Let p, V, T be the total pressure, total volume, Kelvin temperature and U, S, H, F_{VT}, F_{pT}, C_V, C_p be the total energy, entropy, heat content, thermodynamic potentials and heat capacities of a mixture of real gases consisting of n_1, n_2, $\cdots$ moles of the Gases 1, 2, $\cdots$ whose chemical potentials in the mixture are μ_1, μ_2, $\cdots$. Let $C=\Sigma n_i/V$ be the concentration of the mixture; $C_i=n_i/V$ be the concentration of Gas i in the mixture; and $x_i=n_i/\Sigma n_i$ be the mole fraction of Gas i in the mixture.

Let p_{ei}, U_{ei}, S_{ei}, H_{ei}, F_{VTei}, F_{pTei}, C_{Vei}, C_{pei} be the pressure, energy, entropy heat content, thermodynamic potentials, and heat capacities respectively of n_{ei} moles of the pure Gas i ($i=1, 2, \cdots$) existing by itself in the total volume V, at the temperature T and with the chemical potential μ_i; the quantities V, T and μ_i having identically the same values that apply to the gas mixture. Let $C_{ei}=n_{ei}/V$ be the concentration of the pure Gas i.

It is evident that the pure Gas i is in equilibrium with the gas mixture with respect to the isothermal transfer of Gas i from the vessel containing the pure gas to that containing the mixture or from the mixture to the pure gas, the chemical potential of the pure Gas i being kept equal to that of Gas i in the mixture throughout the process; that is, each gas would be in equilibrium with the gas mixture through a semipermeable membrane which permits only that gas to pass through. Hence the quantities with the subscript e will be called the "equilibrium" quantities.

Thermodynamic quantities with the subscript 1 refer to pure gases which are considered without relation to any gas mixture.

3. The Assumptions

Assumption 1: At all temperatures[7] the energy of a real gas differs from a function of the temperature by a quantity which, at constant temperature, approaches zero with the pressure, p in the manner that $\zeta_1 p$ approaches zero with the pressure where ζ_1 and its derivative are bounded.

Assumption 2: At all temperatures[7] the ratio of the equilibrium pressure of each gas in a mixture to the product of the mole fraction of that gas in the mixture multiplied by the total pressure p of the mixture differs from unity by a quantity which, at constant temperature and composition, approaches zero with the total pressure in the manner that $\xi_i p$ approaches zero with the total pressure, where ξ_i and its derivatives are bounded.

[7] This means, of course, for the temperature range for which the resulting thermodynamic relations are to be used. The region in the immediate neighborhood of 0°K is to be excluded.

Thus for all temperatures we may write for low pressures:

$$U_1 = f_1(T) + \zeta_1 p \tag{1}$$

$$\frac{p_{ei}}{px_i} = 1 + \xi_i p \quad (i = 1, 2, \cdots). \tag{2}$$

In Eq. (1) U_1 is the energy of n_1 moles of any pure Gas 1, T the Kelvin temperature and p the pressure of the gas; the function $f_1(T)$ is a characteristic function of the temperature for each gas, and the parameter ζ_1 varies with the temperature. In Eq. (2) p_{ei} is the equilibrium pressure of Gas i, x_i its mole fraction in the mixture and p the total pressure of the mixture; the parameter ξ_i varies with the temperature and composition of the mixture.

At very low pressures (1) and (2) become:

$$U_1^* = f_1(T) \tag{3}$$

$$\left(\frac{p_{ei}}{px_i}\right)^* = 1 \quad (i = 1, 2, \cdots). \tag{4}$$

Thus:

At very low pressures the energy of a pure gas is a function of the temperature alone.

At very low pressures the ratio of the equilibrium pressure of a gas to the product of the mole fraction of the gas in the mixture multiplied by the total pressure of the mixture is unity.

4. The Equilibrium Concentration

For the gas mixture we may write the fundamental equation:

$$Vdp = SdT + n_1 d\mu_1 + n_2 d\mu_2 + \cdots \tag{5}$$

and for each pure gas there is a relation of the type:

$$Vdp_{ei} = S_{ei}dT + n_{ei}d\mu_i \qquad (i = 1, 2, \cdots) \tag{6}$$

where V, dT, $d\mu_1$, $d\mu_2$, $\cdots$ have identically the same values in (5) and (6). From (5) we see that:

$$\left(\frac{dp}{d\mu_i}\right)_{T,\mu} = \frac{n_i}{V}; \qquad \left(\frac{dp}{dT}\right)_{\mu} = \frac{S}{V} \quad (i = 1, 2, \cdots) \tag{7}$$

and from (6):

$$\left(\frac{dp_{ei}}{d\mu_i}\right)_T = \frac{n_{ei}}{V}; \qquad \left(\frac{dp_{ei}}{dT}\right)_{\mu_i} = \frac{S_{ei}}{V} \quad (i = 1, 2, \cdots) \tag{8}$$

The subscript μ to a partial derivative indicates that during the differentiation all of the μ's are held constant, unless the differentiation is with respect to one of the μ's in which case all of the other μ's are held constant.

Eq. (2) can be written:

$$p_{ei} = px_i(1 + \xi_i p) \quad (i = 1, 2, \cdots) \tag{9}$$

Adding the equilibrium pressures for all of the gases in the mixture and placing $\Sigma x_i = 1$, we obtain:

$$\Sigma p_{ei} = p(1 + \xi p) \tag{10}$$

where ξ has been written for $\Sigma x_i \xi_i$. Differentiation of (10) successively with respect to $\mu_1, \mu_2, \cdots$ gives the relations:

$$\left(\frac{dp_{ei}}{d\mu_i}\right)_T = \left(\frac{dp}{d\mu_i}\right)_{T,\mu} (1 + 2\xi p) + p^2 \left(\frac{d\xi}{d\mu_i}\right)_{T,\mu} \quad (i = 1, 2, \cdots) \tag{11}$$

Since:

$$\left(\frac{d\xi}{d\mu_i}\right)_{T,\mu} = \left(\frac{dp}{d\mu_i}\right)_{T,\mu} \left(\frac{d\xi}{dp}\right)_{T,\mu_2,\mu_3,\cdots} \quad (i = 1, 2, \cdots) \tag{12}$$

Eq. (11) may be written:

$$\left(\frac{dp_{ei}}{d\mu_i}\right)_T = \left(\frac{dp}{d\mu_i}\right)_{T,\mu} \left[1 + 2\xi p + p^2 \left(\frac{d\xi}{dp}\right)_{T,\mu_2,\mu_3,\cdots}\right] (i = 1, 2, \cdots) \tag{13}$$

By Assumption 2 the partial derivative in the last term of (13) is bounded, and hence this term is of higher order than $2\xi p$. Replacing the partial derivatives of (13) by use of the relations (7) and (8) we obtain for low pressures the equations:

$$\frac{n_{ei}}{V} = \frac{n_i}{V}(1 + 2\xi p) \quad (i = 1, 2, \cdots) \tag{14}$$

In terms of concentrations (14) becomes:

$$\frac{C_{ei}}{C_i} = 1 + 2\xi p \quad (i = 1, 2, \cdots) \tag{15}$$

and at very low pressures:

$$\left(\frac{C_{ei}}{C_i}\right)^* = 1 \quad (i = 1, 2, \cdots) \tag{16}$$

At very low pressures the ratio of the equilibrium concentration of a gas to its concentration in the gas mixture is unity.

Eq. (16) may be written in a form corresponding more closely to (4):

$$\left(\frac{C_{ei}}{Cx_i}\right)^* = 1 \quad (i = 1, 2, \cdots) \tag{17}$$

5. The Laws of Boyle and Avogadro

Lurie and Gillespie[8] have shown that if Eq. (4) holds at all pressures, then the gases obey the laws of Boyle and of Avogadro. Similar results may be obtained for real gases at very low pressures from the Assumption 2. When the relation (9) for each gas is divided by the corresponding relation (14), we obtain:

$$\frac{p_{ei}V}{n_{ei}}\frac{1}{1+\xi_i p}=\frac{pV}{\Sigma n_i}\frac{1}{1+2\xi p}. \quad (i=1,2,\cdots) \tag{18}$$

Consider that n_{e1}, n_{e2}, $\cdots$ moles of the pure gases 1. 2, $\cdots$ and Σn_i moles of the gas mixture are placed in separate compartments each of volume V and at temperature T, and that the chemical potential of each of the pure gases has the same value during all variations as that which it has in the gas mixture. Let T, μ_1, μ_2, $\cdots$ be taken as the independent variables as in Eqs. (5) and (6). In the following discussion all variations are made at constant temperature. With μ_1 held constant both for the pure gas and the gas mixture we can vary μ_2, μ_3, $\cdots$ thus causing the pressures and concentrations of the Gases 2, 3, $\cdots$ and of the gas mixture to vary. From (6) we see that the first term of (18) for Gas 1 cannot vary except through the factor $(1+\xi_1 p)$, but the effect of this variation can be made as small as desired by carrying out the whole process at sufficiently low pressures. At very low pressures the first term of (18) for Gas 1 may be considered constant during the given variations and hence each of the other terms must have remained constant during the variations. But Gas 2 or any other of the gases could just as well have been chosen as the one whose chemical potential was held constant. Hence for all isothermal variations of the chemical potentials at very low pressures:

$$\left(\frac{p_1V_1}{n_1}\right)^*=\left(\frac{p_2V_2}{n_2}\right)^*=\cdots=\left(\frac{pV}{\Sigma n_i}\right)^*=\text{constant}=F(T). \tag{19}$$

The terms of (19) are each individually constant at constant temperature for gases or gas mixtures each confined in a cylinder. Hence the quantities p_1^*, $(V_1/n_1)^*$, p_2^*, $(V_2/n_2)^*$, $\cdots$ which refer to the Gases 1, 2, $\cdots$ are no longer necessarily equilibrium values. The temperature function F(T) is the same for all of the gases. For very low pressures we may write:

$$\frac{(pV)^*}{n_1}=F(T) \tag{20}$$

for any pure real gas; and:

$$\frac{(pV)^*}{\Sigma n_i}=F(T) \tag{21}$$

[8] Lurie and Gillespie, Jour. Amer. Chem. Soc. **49**, 1146 (1927), See also Gillespie, Phys. Rev., **36**, 121 (1930).

for any mixture of real gases. Hence:

At very low pressures the laws of Boyle and Avogadro hold for all real gases and mixtures of real gases.

At very low pressures the ratio of the pressure to the concentration is the same function of the temperature for all real gases and mixtures of real gases.

Now

$$\left(\frac{dU}{dV}\right)_T = T\left(\frac{dp}{dT}\right)_V - p \tag{22}$$

and from this relation together with (1) and (20) it is evident that at low pressures:

$$\frac{pV}{n_1} = F(T) + \beta_1 p \tag{23}$$

or to the same degree of approximation:

$$\frac{pV}{n_1} = F(T)\left(1 + \frac{n_1\beta_1}{V}\right) \tag{24}$$

where the subscript 1 refers to any pure gas and the parameter β_1 varies with the temperature. Moreover for gas mixtures at low pressures we can evidently write:

$$\frac{pV}{\Sigma n_i} = F(T) + \beta p \tag{25}$$

or to the same degree of approximation:

$$\frac{pV}{\Sigma n_i} = F(T)\left(1 + \frac{\Sigma(n_i)\beta}{V}\right) \tag{26}$$

where the parameter β varies with the temperature and composition of the mixture.

6. Additivity of Certain Thermodynamic Functions

Gibbs[9] has shown that if the pressure of a mixture of gases is equal to the sum of the equilibrium pressures of the component gases then certain thermodynamic quantities are "additive." We can derive similar relations for real gases at very low pressures from the Assumption 2.

Differentiating (10) with respect to the temperature at constant μ_1, μ_2, $\cdots$ we obtain:

$$\Sigma\left(\frac{dp_{ei}}{dT}\right)_{\mu_i} = \left(\frac{dp}{dT}\right)_\mu (1 + 2\xi p) + p^2\left(\frac{d\xi}{dT}\right)_\mu \tag{27}$$

[9] Gibbs, Scientific Papers; Vol. I, p. 157.

which may be written:

$$\Sigma V\left(\frac{dp_{ei}}{dT}\right)_{\mu_i} = V\left(\frac{dp}{dT}\right)_{\mu}\left[1 + 2\xi p + p^2\left(\frac{d\xi}{dp}\right)_{\mu}\right]. \tag{28}$$

The last term is of higher order than $2\xi p$ and may be neglected. Substitution from (7) and (8) into (28), gives for low pressures the result:

$$\Sigma S_{ei} = S(1 + 2\xi p). \tag{29}$$

The energy of the mixture is given by the relation:

$$U = TS - pV + \mu_1 n_1 + \mu_2 n_2 + \cdots \tag{30}$$

and for each pure gas there is a relation of the type:

$$U_{ei} = TS_{ei} - p_{ei}V + \mu_i n_{ei} \qquad (i = 1, 2, \cdots) \tag{31}$$

Adding the Eqs. (31) for all of the gases composing the mixture and making use of the relations (10), (14) and (29), we obtain:

$$\Sigma U_{ei} = TS(1 + 2\xi p) - pV(1 + \xi p) + \Sigma(\mu_i n_i)(1 + 2\xi p) \tag{32}$$

Hence at low pressures:

$$\Sigma U_{ei} = U(1 + 2\xi p) + pV\xi p. \tag{33}$$

From the definitions:

$$H = U + pV \tag{34}$$

$$F_{VT} = U - TS \tag{35}$$

$$F_{pT} = U - TS + pV \tag{36}$$

and the relations already given, we find that at low pressures:

$$\Sigma H_{ei} = H(1 + 2\xi p) \tag{37}$$

$$\Sigma F_{VTei} = F_{VT}(1 + 2\xi p) + pV\xi p \tag{38}$$

$$\Sigma F_{pTei} = F_{pT}(1 + 2\xi p). \tag{39}$$

From (25) we note that at low pressures the quantity pV is bounded. By use of the relations already given and the first and second law equation, it can readily be shown that as the pressure on a gaseous system is isothermally reduced, the energy and heat content are bounded, and that the entropy and thermodynamic potentials approach plus or minus infinity in the same manner as $\pm \ln p$. But:

$$\lim_{p \to 0} p \ln p = 0$$

and hence at very low pressures:

$$\Sigma S_{ei}^* = S^* \tag{40}$$

$$\Sigma U_{ei}^* = U^* \tag{41}$$

$$\Sigma H_{ei}^* = H^* \tag{42}$$

$$\Sigma F_{VT\,ei}^* = F_{VT}^* \tag{43}$$

$$\Sigma F_{pT\,ei}^* = F_{pT}^*. \tag{44}$$

At very low pressures the entropy, energy, heat content, and thermodynamic potentials of a mixture of real gases are equal respectively to the sum of the entropies, energies, heat contents, and thermodynamic potentials of the component gases existing each by itself with the same value of its volume, temperature and chemical potential as in the gas mixture.

Further, it is evident from (16) that the above statement applies when the component gases are each taken with the same value of its volume and temperature as in the gas mixture and with the ratio of its concentration to its concentration in the gas mixture equal to unity.

From (10) and (15) it is evident that at very low pressures:

$$\left(\frac{\Sigma p_{ei}}{p}\right)^* = 1 \tag{45}$$

$$\left(\frac{\Sigma C_{ei}}{C}\right)^* = 1 \tag{46}$$

At very low pressures the ratio of the sum of the equilibrium pressures (or equilibrium concentrations) of the gases composing a mixture to the pressure (or concentration) of the gas mixture is unity.

7. The Energy

From Eqs. (1) and (33), we find that at low pressures the energy of a gas mixture can be written:

$$U = \Sigma f_i(T) + \zeta p \tag{47}$$

where the parameter ζ varies with the temperature and composition of the mixture. Hence:

$$U^* = \Sigma f_i(T). \tag{48}$$

At very low pressures the energy of a mixture of real gases is a function of the temperature and composition.

By use of (24) and (26) we can write (1) and (47) to the same degree of approximation in the more convenient forms:

$$U_1 = f_1(T) + \frac{\zeta_1'}{V} \tag{49}$$

$$U = \Sigma f_i(T) + \frac{\zeta'}{V} \tag{50}$$

where ζ_1' and ζ' have somewhat different numerical values from ζ_1 and ζ.

8. The Pressure-Volume-Temperature Relation

The following treatment is an adaptation of a method which Poincaré[10] used for the case that the relations (3) and (20) hold for all pressures, and which is similar to a method that Phillips[11] applied for the case that the isometrics of a gas are strictly linear. We shall use the relations (49) and (24) which apply to real gases at low pressures, and (50) and (26) which apply to mixtures of real gases at low pressures.

Substitution of (49) into the first and second law equation:

$$dS = \frac{dU}{T} + \frac{p}{T}dV \tag{51}$$

gives:

$$dS = \left[\frac{1}{T}\frac{df_1}{dT} + \frac{1}{TV}\frac{d\zeta_1'}{dT}\right]dT + \left[\frac{p}{T} - \frac{\zeta_1'}{TV^2}\right]dV. \tag{52}$$

Since dS is a complete differential:

$$\frac{\partial}{\partial V}\left[\frac{1}{T}\frac{df_1}{dT} + \frac{1}{TV}\frac{d\zeta_1'}{dT}\right] = \frac{\partial}{\partial T}\left[\frac{p}{T} - \frac{\zeta_1'}{TV^2}\right]. \tag{53}$$

The quantities f_1 and ζ_1' do not vary with the volume, hence:

$$\frac{\partial}{\partial T}\left(\frac{p}{T}\right) + \frac{\zeta_1'}{T^2V^2} = 0 \tag{54}$$

Integration of (54) at constant volume gives:

$$\frac{p}{T} + \frac{1}{V^2}\int \frac{\zeta_1'}{T^2}dT = \Phi\left(\frac{V}{n_1}\right). \tag{55}$$

For all values of the temperature other than zero, Eq. (55) may be written:

$$p = T\,\Phi\left(\frac{V}{n_1}\right) + \frac{n_1^2\kappa_1}{V^2}$$

where κ_1 is bounded. From Eq. (24):

$$p = \frac{n_1}{V}F(T) + \frac{n_1^2\beta_1}{V^2}F(T) \tag{56}$$

whence:

$$\frac{V}{n_1}\Phi\left(\frac{V}{n_1}\right) = \frac{1}{T}F(T) + [\beta_1 F(T) - \kappa_1]\frac{n_1}{VT}. \tag{57}$$

[10] Poincaré, Thermodynamique, Gauthier-Villars, Paris, 2nd ed.; p. 160.
[11] Phillips, Jour. of Math. and Physics **1**, No. 1 (1921).

At very low pressures (57) becomes:

$$\frac{V^*}{n_1}\Phi\left(\frac{V}{n_1}\right)^* = \frac{1}{T}F(T) = \text{constant} = R \tag{58}$$

since a function of the volume can equal a function of the temperature only if each is constant. Hence:

$$F(T) = RT. \tag{59}$$

We would have obtained the same relation by use of Eqs. (50) and (26), and R would have the same value.

Thus Eqs. (23) and (24) for pure gases become:

$$pV = n_1RT + n_1\beta_1 p \tag{60}$$

$$pV = n_1RT\left(1 + \frac{n_1\beta_1}{V}\right) \tag{61}$$

and (25) and (26) for gas mixtures:

$$pV = \Sigma(n_i)RT + \Sigma(n_i)\beta p \tag{62}$$

$$pV = \Sigma(n_i)RT\left(1 + \frac{\Sigma(n_i)\beta}{V}\right). \tag{63}$$

Hence for real gases at very low pressures:

$$(pV)^* = n_1RT \tag{64}$$

and for gas mixtures:

$$(pV)^* = \Sigma(n_i)RT. \tag{65}$$

At very low pressures the pressure-volume product for a real gas or for a mixture of real gases is equal to the product of the total number of moles present multiplied by RT where R is a universal constant and T the Kelvin temperature.

9. The Heat Content

From the relations (1), (34) and (60) we can write for a pure gas at low pressures:

$$H_1 = f_1(T) + n_1RT + \eta_1 p \tag{66}$$

where η_1 and its temperature derivative are bounded. Moreover from (47), (34) and (62), there results for a gas mixture at low pressures the relation:

$$H = \Sigma f_i(T) + \Sigma(n_i)RT + \eta p. \tag{67}$$

In (66) and (67), $f_1(T)$ (or $f_i(T)$) is the same function of the temperature as that which occurs in (1). At very low pressures (66) and (67) become:

$$H_1^* = f_1(T) + n_1RT \tag{68}$$

$$H^* = \Sigma f_i(T) + \Sigma(n_i)RT. \tag{69}$$

10. The Heat Capacities at Constant Volume and at Constant Pressure.

Differentiation of (49) and (50), and of (66) and (67) according to the relations:

$$C_V = \left(\frac{dU}{dT}\right)_{V,n} \tag{70}$$

$$C_p = \left(\frac{dH}{dT}\right)_{p,n} \tag{71}$$

respectively, where the n denotes differentiation at constant composition, gives:

$$C_{V_1} = \frac{df_1(T)}{dT} + \frac{1}{V}\frac{d\zeta_1'}{dT} \tag{72}$$

$$C_V = \Sigma\left(\frac{df_i(T)}{dT}\right) + \frac{1}{V}\frac{d\zeta'}{dT} \tag{73}$$

$$C_{p_1} = \frac{df_1(T)}{dT} + n_1 R + \frac{d\eta_1}{dT}p \tag{74}$$

$$C_p = \Sigma\left(\frac{df_i(T)}{dT}\right) + \Sigma(n_i)R + \frac{d\eta}{dT}p \tag{75}$$

in which C_{V_1} and C_{p_1} refer to pure gases, and C_V and C_p to gas mixtures. Moreover it is evident that at low pressures:

$$C_{p_1} - C_{V_1} = n_1 R + \alpha_1 p \tag{76}$$

$$C_p - C_V = \Sigma(n_i)R + \alpha p \tag{77}$$

where α_1 and α are bounded. At very low pressures the relations (72) to (77) become:

$$C_{V_1}^* = \frac{df_1(T)}{dT}; \qquad C_{p_1}^* = \frac{df_1(T)}{dT} + n_1 R \tag{78}$$

$$C_V^* = \Sigma\frac{df_i(T)}{dT}; \qquad C_p^* = \Sigma\left(\frac{df_i(T)}{dT}\right) + \Sigma(n_i)R \tag{79}$$

$$C_{p_1}^* - C_{V_1}^* = n_1 R \tag{80}$$

$$C_p^* - C_V^* = \Sigma(n_i)R. \tag{81}$$

At very low pressures the heat capacities at constant volume and at constant pressure of a real gas are functions of the temperature, and those of mixtures of real gases are functions of the temperature and composition.

At very low pressures the difference between the heat capacity at constant pressure and at constant volume for a real gas or for a mixture of real gases is

equal to the product of the total number of moles present multiplied by the universal gas constant R.

From (78) and (79) it is evident that at very low pressures:

$$C_V^* = \Sigma C_{V_i}^* \tag{82}$$

$$C_p^* = \Sigma C_{p_i}^* \tag{83}$$

11. Summary of the Relations for Very Low Pressures

It has been shown that the two assumptions for low pressures:

$$U_1 = f_1(T) + \zeta_1 p \tag{1}$$

$$\frac{p_{ei}}{p x_i} = 1 + \xi_i p \tag{2}$$

together with the general laws of thermodynamics are the necessary and sufficient conditions for the following relations to hold at very low pressures:

Relations for real gases		*Relations for mixtures of real gases*	
$(pV)^* = n_1 RT$	(64)	$(pV)^* = \Sigma(n_i)RT$	(65)
$U_1^* = f_1(T)$	(3)	$U^* = \Sigma f_i(T)$	(48)
$H_1^* = f_1(T) + n_1 RT$	(68)	$H^* = \Sigma f_i(T) + \Sigma\,(n_i)RT$	(69)
$C_{V_1}^* = \dfrac{df_1(T)}{dT}$	(78)	$C_V^* = \Sigma \dfrac{df_i(T)}{dT}$	(79)
$C_{p_1}^* - C_{V_1}^* = n_1 R$	(80)	$C_p^* - C_V^* = \Sigma(n_i)R$	(81)

Equilibrium relationships		*Additive relationships*[12]	
$\left(\dfrac{p_{ei}}{p x_i}\right)^* = 1$	(4)	$\left(\dfrac{\Sigma p_{ei}}{p}\right)^* = 1$	(45)
$\left(\dfrac{C_{ei}}{C_i}\right)^* = 1$	(16)	$\left(\dfrac{\Sigma C_{ei}}{C}\right)^* = 1$	(46)
$\left(\dfrac{C_{ei}}{C x_i}\right)^* = 1$	(17)	$S^* = \Sigma S_{ei}^*$	(40)
		$U^* = \Sigma U_i^*$	(41)
		$H^* = \Sigma H_i^*$	(42)
		$F_{VT}^* = \Sigma F_{VT\,ei}^*$	(43)
		$F_{pT}^* = \Sigma F_{pT\,ei}^*$	(44)
		$C_V^* = \Sigma C_{V_i}^*$	(82)
		$C_p^* = \Sigma C_{p_i}^*$	(83)

[12] When a thermodynamic quantity is bounded as the pressure approaches zero, it is not necessary to include the subscript *e* since in the region of very low pressures the value of the quantity does not change appreciably with pressure.

It is evident from the derivations given that each of the above relations holds at infinitely low pressures. Hence in each of these relations we may consider that the asterisk denotes "the limit of the quantity (to which the asterisk is attached) as the pressure on the system approaches zero at constant temperature, and subject to certain restrictions on the concentrations of the components." When no chemical reaction between the components of the system is contemplated, the restriction is simply that the composition of the system does not vary; when chemical reaction occurs the restriction is that the system be always maintained in equilibrium, and in this case a variation in composition will occur as the limit is approached. Thus for example, we may write:

$$\lim_{p \to 0} pV = n_1 RT \qquad \lim_{p \to 0} \frac{p_{ei}}{p x_i} = 1$$

$$\lim_{p \to 0} U_1 = f_1(T) \qquad \lim_{p \to 0} S = \Sigma \lim_{p \to 0} S_{ei}$$

$$\lim_{p \to 0} (C_{p_1} - C_{V_1}) = n_1 R$$

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Breadth of Compton Modified Line

Professors Ross and Clark of Stanford, using the ingenious balanced filter method of Ross, have investigated the shifted line in the Compton effect for antimony, $K\alpha_1$ and $K\alpha_2$, lines scattered from beryllium. In this method the scattering angle is varied so as to vary the shift of the modified line. The scattered radiation is observed with an ionization chamber after passage through a silver filter and then a palladium filter balanced against the silver filter. The difference between the transmissions plotted as a function of the scattering angles exhibits peaks or fluctuations in the curve at the scattering angles of 55° and 75° corresponding to the points at which the shifted lines from $K\alpha_1$, $K\alpha_2$, respectively cross the silver edge of the spectral region defined by the balance filter method.

In view of the fact that the author has published experimental results[1] in which the breadth of the Compton line from molybdenum, $K\alpha_1$, $K\alpha_2$ scattered at nearly 180° from beryllium is too great to permit resolving the α_1, α_2 peaks, it seems worth while pointing out that these two results are not necessarily discordant. The author's experimental results were accompanied with his theory of the breadth and structure of the Compton line according to which a prominent part of Compton line structure, due to scattering by the free or conduction electrons in metallic scatterers, has a breadth which can best be correlated with the velocities of these electrons required by the Fermi statistics and which furnishes confirmatory evidence of the correctness of the Fermi distribution of velocities for conduction electrons in contradistinction to the older Boltzmann statistics.

According to the author's theory, the breadth of the Compton line, however, depends not only on the velocity distribution of conduction electrons, but also on the primary wave-length used and on the angle of scattering. In fact, for any given velocity β of randomly moving conduction electrons, the author's theory asserts that the contribution to the Compton line is a small rectangular element having a spectral breadth given by (formula (1), page 647)

$$\Delta\lambda = 4\beta\lambda^*.$$

In this formula, which gives the breadth of the Compton line as a function of scattering angle, the symbol λ^* stands for a wave-length which is defined thus:

$$2\lambda^* = (\lambda_c^2 + \lambda_1^2 - 2\lambda_c\lambda_1 \cos\theta)^{\frac{1}{2}}$$

λ^* is most easily visualized by a diagram. Construct a triangle, one angle of which equals the scattering angle, and having the two adjacent sides to this angle proportional respectively to the primary wave-length λ_1, and the shifted wave-length λ_c, of the simple Compton theory, for initially stationary electrons. Then the third side of this triangle is proportional to $2\lambda^*$.

On the basis of this formula, the author has computed for the case of Ross' experiment

$\theta = 75°$, $\lambda_1 = 469$ X.U., $\lambda_c = 485$ X.U., $\lambda^* = 292$ X.U.

$\theta = 55°$, $\lambda_1 = 474$ X.U., $\lambda_c = 485$ X.U., $\lambda^* = 222$ X.U.

If one assumes in beryllium *one* conduction electron per atom, this would give a Compton line breadth for Ross' cases of 6.5 and 5X-units, respectively. This refers to the breadth of the line at the base of the part contributed by conduction electrons, which according to the author's calculation seems to come a little below half maximum value. Assuming

[1] J. W. DuMond, Phys. Rev., **33**, 643–658 (1929).

two conduction electrons per atom, the corresponding breadths for Ross' cases are 8.4 X.U. and 6.36 X.U. respectively. It seems, therefore, safe to conclude that Ross' resolution of the doublet in the shifted radiation is for the conditions of his experiment not necessarily inconsistent with either the author's theory of Compton shifted line structure or with his published experimental observations.

At the present writing the author, in collaboration with Mr. H. A. Kirkpatrick, has just succeeded in obtaining photographic spectrograms of the Compton shifted line, using Mo $K\alpha_1$, α_2 scattered at 90° from graphite with a maximum inhomogeneity of scattering angle of less than one degree. The unmodified doublet is completely resolved on the negative and the Compton line appears very broad and diffuse. This work is being done with the fifty-crystal spectrograph described in Review of Scientific Instruments, Vol. 1, No. 2, February 1930.

The author believes that this new instrument at last affords the possibility of investigating the whole question of Compton modified radiation under adequately pure conditions of scattering angle and spectral resolution. We feel that we can now announce with complete assurance that the Compton shifted line is more diffuse than the lines of the primary radiation.

J. W. M. DuMond

California Institute of Technology,
Pasadena, California,
June 20, 1930.

The Raman Effect in Trimethylethylene

In some experiments made a year ago on the Raman effect in trimethylethylene several diffuse modified lines were found. The stronger correspond to infrared wave-lengths $3.44 \pm 0.05\mu$ and $8.4 \pm 0.2\mu$. Several fainter lines were found between these two. An anti-Stokes line corresponding to 8.4μ was also faintly seen excited by the mercury line 4358A. It seems probable that all these lines can be matched by absorption lines belonging to the group CH although no absorption line was found recorded as long as 8.4μ.

Accidental contamination with rubber added a continuous scattering, with a marked denser band beginning near the position of the strongest line, *ca* 4600A. A continuous spectrum was obtained in about the same position when a little rubber was dissolved in carbon tetrachloride, making it probable that the effect was due to the rubber and not to a change in viscosity of less than one percent. In this case a suggestion of a second very broad band with maximum about 5500A was also found. If these bands were due to Raman scattering it would be necessary to think of the exciting mercury lines as 4046A and 3650A. The light appeared to be partially polarized.

DOROTHY FRANKLIN
E. R. LAIRD

Mount Holyoke College,
June 14, 1930.

Photoionization of Salt Vapors

The chief interest presented by the photoionization of the vapors of various compounds is that it may afford additional information regarding the structure of molecules. As far as I am aware no such work with the vapors of simple inorganic salts has as yet been done.

In an investigation undertaken by me on these lines with the vapors of halides of various metals, a marked photoionization of these vapors was observed. The illumination was produced by intense ultraviolet light of wave-lengths longer than 1850A. The photoeffect from the electrodes and the walls was negligibly small as compared with the photocurrent from the vapor, in some cases the latter was a hundred times as great as the photocurrent which could be produced by direct illumination of the electrodes.

On raising the temperature of the salt thermal ionization currents could be observed without illumination, an effect which has been previously extensively studied by G. C. Schmidt and his co-workers (Ann. d. Physik **82,** 664 (1927) **2,** 313 (1929)). The photoionization begins generally at much lower temperatures than the temperatures at which the thermo-current is noticeable.

The salts studied first were TlI, TlBr, TlCl. It has been previously shown in this laboratory (Butkow and Terenin, Zeits. f. Physik **49,** 865 (1928), Butkow, ibid. **58,** 232 (1929)) that the excitation energy of the first

electronic level of these molecules coincides very closely with the corresponding value for the Tl atom; the figures (in volts) are as follows: 3.4 for TlI, 3.6 for TlBr and 3.8 for TlCl as against 3.3 for Tl. It seems therefore that the Tl atom has to some extent an individual existence in the molecule and can be excited by light absorption independently of the other component, a view consistent with the fact that these molecules are "atomic" ones.

There arose naturally the question, whether the value of the ionization energy of the molecule would coincide with the ionization potential of Tl. The experiment showed, in fact, the existence of a strong photoionization of these vapors, the active wave-lengths lying on the short wave-length side of certain limits, which are 2140A for TlI and 2070A for TlBr. Expressed in volts this gives for the assumed ionization potentials of TlI and TlBr, 5.8 and 6.0 respectively, whereas the ionization potential of Tl is 6.1 V.

The agreement is sufficiently good to support the view that at these wave-lengths the ionization of the TlX molecules sets in, as the result of the liberation of an electron from the Tl atom. An explanation of the photocurrent by the dissociation of the TlX molecules into ions Tl^+ and X^-, improbable in itself, would give other threshold values than is the case here. It must be noticed that the range of ionizing radiation overlaps to some extent the range of wave-lengths producing the dissociation of the TlX molecules with subsequent emission of certain Tl lines, which has been thoroughly studied before (Terenin, Zeits. f. Physik **44**, 713 (1927); Butkow and Terenin, loc. cit.). The wave-length thresholds of these two processes are, however, quite different.

From the known equation: $D_m + I_a = I_m + D_{m+}$, where I_a, I_m are the ionization energies of the Tl atom and the TlX molecule respectively, D_m, D_{m+}—the dissociation energies of the neutral and the ionized molecule, the value of D_{m+} can be computed to be 2.8V for TlI^+ and 3.3V for $TlBr^+$. As the dissociation energies D_m of the neutral molecules are 2.5 and 3.2V respectively, it may be concluded that the molecular ions TlX^+ are more stable than the corresponding neutral molecules; this fact, interesting in itself, is consistent with other known data.

For TlCl the threshold was found to be 1860A, but this value is not quite certain owing to a dubious origin of the salt used in the experiment.

A marked decrease of the photosensitivity in the sequence TlI, TlBr, TlCl was noticed.

On raising the applied voltage from 50 to 600 V, the appearance of Tl arc lines could be observed in TlI, but only during the illumination of the vapor. This can be explained as an excitation of the Tl atoms always present in the vapor, by the photoelectrons liberated from the molecules and accelerated by the field applied. There is, besides, the possibility of various dissociation and excitation processes induced in TlI by these electrons.

Other volatile halides, e.g. AgI, PbI_2, $PbCl_2$, BiI_3, were also investigated, but they gave much smaller photoionization currents, than the Tl halides. In HgI_2 and CdI_2 no measurable effect could be observed.

The possibility of a photoionization seems to be dependent chiefly on the magnitude of the ionization potential of the metallic atom in the molecule, which must fall within the range of the ultraviolet frequencies used. The photoionization is more pronounced in the iodides and decreases in magnitude in the chlorides.

The magnetic mass analysis of the ions produced under various circumstances will facilitate, I hope, to a great extent the interpretation of the underlying processes.

A. TERENIN

Optical Institute,
Leningrad, Russia,
May 24, 1930.

The Raman Effect in Solutions of Sodium Nitrate of Varying Concentration

Experiments suggested by those of Rao on HNO_3 (Nature, **124**, 762 (1929)) have been made on the Raman spectrum of $NaNO_3$ at concentrations of 5, 10, and 30 percent and saturated. Exposures were made varying approximately inversely with the concentration from 39 hours down. The source of light was a glass mercury arc, and the spectrograph a Hilger D78. The Raman line with frequency difference 1049 ± 6 cm^{-1} was found excited by the mercury lines 4358, 4077, and 4046, approximately equally strongly in the different cases, and no new lines were found either in the more dilute or in the saturated solution.

This remained true when the time of exposure for the saturated solution was increased to 15 hours. This line agrees with that found by Carrelli, Pringsheim and Rosen, (Zeits. f. Physik **51**, 511 (1928)) and is attributed to the NO_3 ion, since they found it in solutions of different salts containing this ion. The present experiment confirms this and shows no indication of $NaNO_3$ molecules, although from conductivity measurements the partial dissociation theory would have said that nearly two-thirds of the salt was nondissociated in the saturated solution.

The water band was also found excited by the mercury lines 4358, 4077, 4046, and 3650. The water was redistilled. The ordinary laboratory distilled water spectrum showed many lines, a number appearing like absorption lines although a photograph of the absorption in the region showed nothing. These lines could not be attributed to Raman scattering. The redistilled water spectrum showed only the water band in the region of wave-lengths shorter than 5460A except once a faint suggestion of an absorption line at 4859A, several lines still appeared at wave-lengths greater than 5790A.

VERA STERLING
E. R. LAIRD

Mount Holyoke College,
June 14, 1930.

The Calculation of Energy Values

A number of modifications of the Ritz method of calculating characteristic numbers have recently been applied to the quantum dynamical problem. I have tried another of these methods, which seems to possess several advantages.

The characteristic functions of an atomic system of N electrons whose coordinates are $(r_1, r_2 \cdots)$ are approximated by polynomials of the requisite symmetry,[1] whose separate terms are of the type

$$u(\alpha, r_1)\, v(\beta, r_2) \cdots .$$

Taking a hint from the empirical formulae for energy levels, I assume that each of these functions, say v, is a characteristic function of a one-electron system whose nuclear charge is, say, β. These various "effective" charges $\alpha, \beta, \cdots$, are then determined so that the variation integral is a minimum, subject to the condition that the wave function is of the form just described. The justification for this choice of wave function is purely empirical at present, but it is believed that some theoretical justification for it may be found.

The rule has several advantages: (1) the approximate wave function involves at most N parameters. Others have often used more without obtaining results that are much more accurate than those given by the present choice. (2) It leads to a definite result for the approximate wave function, no matter what the atomic system under consideration may be. (3) Many of the integrals whose numerical values are needed have a simple form. (4) The same functions $u, v \cdots$, recur in many different problems, so that when the numerical work required for one has been finished, much of the work for several others is also completed. This will be particularly true in the later parts of the periodic system.

The method has already been applied to the particular case of the normal states of atoms of two electrons,[2] the result being

TABLE I

Z	Level	$T/(Z-1)^2$			$\alpha(1s)$	$\beta(2p)$
		Present method	Perturb. theory	Observ.		
2	He I, 2^1P	0.245	−0.039	0.2475	2.003	0.965
2	He I, 2^3P	0.262	+0.097	0.2657	1.99	1.09
3	Li I, 2^1P	0.245	0.173	0.250	3.007	1.94
3	Li I, 2^3P	0.261	0.224	0.263	2.98	2.16

[1] This has also been suggested by V. Guillemin and C. Zener, Zeits. f. Physik **61**, 199 (1930).

[2] J. Frenkel, Einführung in die Wellenmechanik, p. 291 ff. Berlin, J. Springer (1930).

that their term values are $2(Z-5/16)^2$, Z being the true nuclear charge. I have extended the calculations to the $2P$ and $3D$ states with the following results.

In Table I, T is the term value in units of Rh cm^{-1}; the third column contains the result of a calculation based on the foregoing rule; the fourth, the first-order result of perturbation theory; the fifth, the observed value. The quantities α and β are the effective nuclear charges for the $1s$ and $2p$ electrons, respectively. In the case of the $3D$ states, the screening constant $s-\beta$ proves to be so nearly unity that the Balmer formula may be used to calculate the absolute magnitude of the term value. The difference 3^3D-3^1D may be calculated, however, and is compared with the results of perturbation theory and observation in Table II.

TABLE II. 3^3D-3^1D

	Present method	Perturb. method	Observation
He I	5.14×10^{-5}	$198.\times10^{-5}$	3.68×10^{-5}
Li II	3.80×10^{-5}	$30.\times10^{-5}$	2.68×10^{-5}

Having performed the calculations required for the foregoing cases, it was less than two hours' work to compute the following data for the sequence of three-electron systems. A graphical method of interpolation was used, which is believed to have been sufficiently accurate. Although there are systematic deviations of the calculated from the observed values of $T/(Z-2)^2$, it is interesting to note that both sequences show a flat maximum near Be II. The calculated values of the screening constants $Z-\beta$ are not strictly comparable with those deduced from the observed doublet separation, but both sequences decrease monotonically.

Theory indicates that the method should be applicable to the 2^3S state of atoms with two electrons, but requires a slight modification for the 2^1S. A rough calculation verifies this. As soon as the calculations for these states have been made, it will be possible to calculate the normal states of the Li I sequence with very little additional labor. A more detailed account of this investigation will be published later.

TABLE III. $2P$ levels.

	$T/(Z-2)^2$		$Z-\alpha$*	$Z-\beta$ (calc.)	$Z-\beta$ (observ.)
	Present Method	Observation			
Li I	0.255	0.2605	0.31	1.98	2.019
Be II	0.258	0.2620	0.32	1.95	1.937
B III	0.258	0.2609	0.32	1.93	1.884
C IV	0.257	0.2595	0.32$_5$	1.91	1.858
N V	0.257		0.33	1.89	1.838
O VI	0.256		0.33	1.88	1.816

* Cf. Guillemin and Zener, reference 1.

CARL ECKART

Ryerson Physical Laboratory,
June 12, 1930.

Some Pecularities of the Spectrum of the Tungsten Mercury Arc

In the course of an investigation of sources of ultraviolet radiation, it was found that the new General Electric Sunlamp in a quartz bulb gives a very intense continuous spectrum in the region from 4000A to 2100A. The source of the ultraviolet radiation is a 300 watt alternating current mercury arc between hot tungsten electrodes with the bulb containing about 100 mm pressure of argon. With a Hilger E2 quartz spectrograph, an exposure of 10 to 15 seconds is sufficient to give an intense continuous background. The intensity of the continuous spectrum relative to the line spectrum can be increased by

burning the lamp at a higher voltage or by increasing the pressure of the mercury vapor in the lamp by external heating.

When the temperature of the mercury is increased, the mercury vapor absorption bands appear. The band at 2540A, first described by R. W. Wood (Astrophys. J., vol. 26), is approximately 0.1A wide at a mercury temperature of 220°C (corresponding to a vapor pressure of 32 mm), and spreads toward longer wave-lengths until it reaches about 2576A at 407°C and 2652A at 426°C, (corresponding to a vapor pressure of 2316 mm). Wood found that this band did not extend beyond the resonance line on the short wave side. Our work with this arc, however, shows the resonance line disappearing at approximately 350°C and two narrow absorption bands appearing at approximately 2534A and 2532A. With further increase in the temperature of the mercury these bands merge with the 2540 band until at 426°C there is continuous absorption between 2530A and 2652A, with evidence of further absorption beyond 2652A.

The five fluted bands around 2345A appear between 320°C and 340°C and broaden as the temperature is increased until they extend over a range of about 16A at 420°C. The broadest of the bands is about 3A wide. The increased pressure also affects certain lines in the region between 3500A and 2100A, some of the lines disappearing entirely at the higher temperatures.

Mercury in a separate quartz absorption cell shows a somewhat different absorption spectrum. The band at 2540A spreads toward the long wave-lengths as the vapor pressure increases until at a temperature of 456°C there is strong absorption of the radiation to 2652A and partial absorption to 2850A, and at 492°C (corresponding to a vapor pressure of 5420 mm) there is strong absorption to 2753A. The band does not extend beyond the resonance line on the short wave side. The fluted bands at 2345A appear at about 340°C and spread to either side until at 460°C the line at 2345A disappears and at 517° (corresponding to a vapor pressure of 7430 mm) the absorption between 2301A and 2350A appears to be continuous.

Further investigation of the absorption bands of both the excited and the unexcited mercury vapor is being made.

W. E. Forsythe
M. A. Easley

Lamp Development Laboratory,
Incandescent Lamp Department,
General Electric Company,
Cleveland, Ohio,
June 10, 1930.

Experimental Evidence for the Existence of Quadrupole Radiation

Rubinowicz (Zeits. f. Physik **53**, 267 (1929)) has shown that spectral lines which violate the transition rule for l or j cannot be explained as dipole radiation, but must be attributed to multipole radiation.

Besides the nebular lines identified by Bowen, the best known line of this type is the green auroral line 5577A. According to McLennan the auroral line is the forbidden combination between the low metastable O I terms $^1S_0$ and $^1D_2$. (The values of these terms have been accurately determined as $^1S_0=76037$ and $^1D_2=93962$ by one of the authors (F.) and will appear shortly in the Phys. Rev.)

Assuming that the auroral line is quadrupole radiation, Rubinowicz (Zeits. f. Physik **61**, 338 (1930)) pointed out that not only those Zeeman components may be observed which correspond to the usual transition $\Delta m=\pm 1$, 0, but also components which correspond to the transitions $\Delta m=\pm 2$. The latter have zero intensity when viewed longitudinally and were therefore not observed by McLennan and Sommer. According to Rubinowicz all of the above transitions show the same intensity when viewed perpendicularly to the field, with the exception of $\Delta m=0$, which can only be observed at oblique angles with the field. Measurements of the transversal Zeeman effect thus make possible an experimental test for the existence of quadrupole radiation.

We have photographed the transversal Zeeman effect of the auroral line. The magnetic field was produced by a large solenoid previously constructed and calibrated by one of us (C.) for a precision determination of e/m by the Zeeman effect. With this solenoid it is possible to maintain a field of 7000 gauss continuously. The auroral line was produced by a d.c. discharge of 0.6 amperes through a mixture of argon and oxygen in a tube 30 mm in diameter. The tube

was silvered over the central portion to increase the intensity by multiple reflection. The light leaving the tube transversally through a slit in the silvering was reflected out of the solenoid by a 45° prism. The Zeeman pattern was photographed with a Fabry-Perot interferometer crossed with a prism spectrograph. By placing a thin calcite plate with proper orientation behind the spectrograph slit, each spectral line appeared separated into its π and σ components.

At a field of 2580 gauss and an interferometer separation of 0.6159 cm, the auroral line was resolved into four components. The displacement of the inner components was $0.92\Delta\nu_{norm}$, that of the outer components was $1.96\Delta\nu_{norm}$. The theoretical factors are 1 and 2, respectively. As was predicted the undisplaced line did not appear. We found that the outer components were polarized perpendicular to the field, and that the components displaced by $\Delta\nu_{norm}$, which in the normal effect are polarized perpendicular to the field, are in this case polarized parallel. This is in complete agreement with the theory of Rubinowicz.

We intend to investigate the Zeeman effect of other forbidden lines.

RUDOLF FRERICHS
J. S. CAMPBELL
Norman Bridge Laboratory of Physics,
California Institute of Technology,
Pasadena, California,
June 9, 1930.

Mobility of Na^+ Ions in H_2

The results of studies of mobilities of ions in mixtures showing the great importance of traces of impurities on mobilities,[1] the studies of Erikson[2] on the change of mobilities of positive ions with age at atmospheric pressures including the effects of impurities, and the prominence recently given the change of charge of initially ionized atoms and molecules in gases reported by Kallman and Rosen,[3] indicating as previously emphasized the total ignorance as to the nature of the ionized carrier,[4,1] led to the present investigations the first results of which it is desired to report at this time.

It seemed essential by as nearly an absolute a method as possible to measure the mobilities of a type of initially ionized carrier which would only reluctantly alter its charge in gases of reasonable purity over very short time intervals. To this end it was attempted to measure the mobilities of positive Na^+ ions from a Kunsman[5] source, using a high frequency square wave form oscillator in fairly pure gases at low pressures. From the nature of the Kunsman sources the gas chosen was hydrogen purified by a process previously used by the writer.* A Kunsman source of positive ions with a square wave form oscillator, using the original Rutherford A.C. method with positive ions instead of negative ions, should: (1) give absolute values of the mobilities with no disturbing effects of gauzes as encountered in other A.C. methods,[6] and with ions definitely emerging from one plane of the parallel plate electrode system; (2) give ions which retain their positive charge in H_2 because of their low ionization potential; and (3) be capable of extension to very short time intervals. The chamber used was a brass one of a type previously described[7] with electrodes altered to suit the Kunsman source. The source was a coating of Na catalyst, kindly sent the writer by Dr. Kunsman, on a thin Pt foil, spot welded onto a small oven of Ni containing a Pt spiral heating element insulated from it by "Insolute" cement. In practice it was heated to about 700°C and gave a copious supply of + ions. It was mounted in the center of the upper plate of a parallel plate condenser in the gas, the lower plate going to ground through an electrometer system. The plate distance was 1.2 cm. By means of an oscillator first designed by J. L. Bowman,[8] built here by Mr. J. E. McVay and adapted by the writer, good square wave form alternating potentials of from 10 to 150 volts with frequencies varying from 500 to 25,000 cycles per second have been achieved. It is probable that the upper frequency limit can be considerably extended. The first results covered a range of pressures from 0.5 to 7 cm of Hg and appeared of sufficient importance to report at this time, as the work will be interrupted for the period of a month or two by external demands on the writer.

Mobilities in H_2 were observed, beginning

* The H_2 was passed over hot Cu, NaOH, $CaCl_2$, two meter long tubes of P_2O_5 and a special double liquid air trap immersed in liquid air.

at between 8 and 10 cm/sec. per volt/cm for + ions at the lower frequencies, (500 cycles to 2000). Above frequencies of 2000 cycles the values of the mobilities increased, reaching a maximum of about 21 cm/sec. per volt/cm above 5000 cycles and remaining there up to 25,000 cycles. Between the lower and higher frequency values the curves indicated by their slopes the probable existence of two carriers present in varying proportions, which made the accurate assignment of mobilities uncertain. This uncertainty will have to remain until the new and somewhat difficult techniques involved shall have been perfected. Hence the results can be considered only as preliminary. The reduced mobility depends primarily on frequency and does not appear to depend on pressure. The correction of the results for temperature was not attempted, first, because the temperature correction for mobility is very uncertain[9] and, secondly, it was not desired to encumber this already complex apparatus at this stage with the necessary added refinements. Since this work was done at constant density the temperature effects will not be great.

The results indicate that Na^+ ions in H_2 within 2×10^{-3} seconds (reciprocal of twice the frequency) after liberation have a little more than double the value of the mobility of the normal ions. These are probably the Na^+ atoms moving in the gas and impeded by their electrostatic attractions only. In 10^{-3} seconds these ions have in part either exchanged charges with other molecules or attached to molecules of H_2, H_2O vapor (present in traces), or some other molecules to form molecular ions. Their mobility is of the order to be expected of the normal positive ions in H_2 as measured by an absolute method.[6] The process (judging from the nature of the curves) appears to be a process similar to that observed by Erikson[3] in his ageing experiments, that is a process which takes place in a single step. The present results differ from Erikson's in the much greater change in mobility occurring, an action which could be ascribed to the use of initial relatively stable Na^+ ions.

Note: Temperature measurements made since this letter indicate average temperatures of less than 130°C in the gas space between the plates. This lowers the average density by a factor of about 0.7 between the plates and indicates that all mobility values reported may be too high in absolute magnitude by a factor less than 1.43. It does not alter the relative changes with frequency.

LEONARD B. LOEB

Physical Laboratory,
University of California,
Berkeley, California,
June 4, 1930.

[1] L. B. Loeb, Phys. Rev. **32,** 81 (1928) and **35,** 192 (1930).
[2] H. A. Erikson, Phys. Rev. **33,** 403 and **34,** 635 (1929).
[3] Kallman and Rosen, Zeits. f. Physik. **58,** 52 (1929) and **61,** 61 (1930).
[4] Loeb and Marshall, Jour. Franklin Inst. **208,** 386 (1929).
[5] C. H. Kunsman, Phys. Rev. **25,** 892 (1925).
[6] L. B. Loeb, Jour. Franklin Inst. **196,** 537 and 771 (1923).
[7] Loeb and Cravath, Jour. Opt. Soc. Am. **16,** 191 (1928).
[8] J. L. Bowman, Phys. Rev. **24,** 31 (1924).
[9] L. B. Loeb, Internat. Crit. Tables, **VI,** 114 (1929).

The Interaction Between Excited and Unexcited Hydrogen Atoms at Large Distances

Eisenschitz and London[1] have recently pointed out that when two similar atoms in different quantum states interact with one another a first order calculation of their mutual energy yields an inverse R^3 term corresponding to a dipole interaction. This term is the controlling one for large values of the internuclear distance R and may yield an energetic order for the different molecular terms at large distances quite different from that which occurs at short distances. As an example they cite the two quantum II states of the hydrogen molecule whose potential energy curves were computed in first order approximation by Kemble and Zener.[2] For small internuclear distances the energetic order of the states is $H_{11}^{12}>H_{10}^{10}>H_9^9>H_{11}^{11}$ as shown by Kemble and Zener, while for large distances the predominance of the $1/R^3$ term leads to the energetic order

[1] Eisenschitz and London, Zeits. f. Physik **60,** 491 (1930).
[2] Kemble and Zener, Phys. Rev. **33,** 512, (1929).

$H_{12}^{12} \leqq H_9^9 > H_{10}^{10} \leqq H_{11}^{11}$. The state $U_9(^1\Pi_+$ in the notation of Eisenschitz and London) whose potential energy curve shows a marked minimum in the region of small values of R has a positive energy of interaction for large values of R corresponding to a repulsive force between the atoms. Similarly the state $U_{10}(^1\Pi_-)$ which shows marked repulsion at short distances, yields a weak attraction at very large distances.

As the computations of Kemble and Zener were not extended to internuclear distances larger than $R=4$ (here the unit of distance is the radius of the innermost Bohr orbit for the H atom) Eisenschitz and London made a necessarily crude interpolation between the asymptotic $1/R^3$ formula and the curves

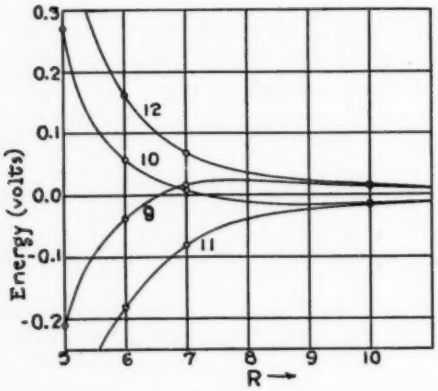

Fig. 1.

given by Kemble and Zener for short distances. This interpolation enabled them to estimate the positions and values of the minimum point in the H_{10}^{10} curve and the maximum in the H_9^9 curve. At London's suggestion, however, the writers have now extended the exact first order computations of Kemble and Zener to the internuclear distances $R=5, 6, 7, 10$. The results are shown in the accompanying table and figure.

The curves show that the crossing-point of the "potential" energy curves for the states *9* and *10* occurs farther out than supposed by Eisenschitz and London. Also the maximum in the potential energy of the state *9* and the minimum for the state *10* are less pronounced than their interpolation would indicate, being almost imperceptible when plotted on the scale of the original graph of Kemble and Zener.

TABLE I

R	H_9^9	H_{10}^{10}	H_{11}^{11}	H_{12}^{12}
	(volts above E_0)			
5	−0.21	0.27	−0.44	0.43
6	−0.038	0.057	−0.181	0.162
7	0.016	0.008	−0.081	0.068
10	0.014	−0.014	−0.016	0.016

In the course of the computation here reported we have found the following misprints in the paper of Kemble and Zener.

Errata to paper by Kemble and Zener, Phys. Rev. **33**, 512 (1929).

p. 525, Eq. (28): the second term in square brackets should be multiplied by 1/4 to read

$$\frac{1}{4}\left(1+R+\frac{R^2}{3}\right)\left(1+\frac{R}{2}+\frac{R^2}{12}\right)$$

p. 526, Eq. (29): the sign of the third term in the right hand member should be positive.

p 530, Eq. (35): should read

$$K_2^{(2)}=\frac{R^4}{3840}\int_1^\infty(\lambda^2-1)(\lambda^3+1/7)\Big\{(3\lambda+R)e^{-3\lambda R/2}$$
$$-\left(\frac{3\lambda^2-1}{2}\right)e^{-\lambda R/2}\left[S'Ei\{-(\lambda+1)R\}-SEi\right.$$
$$\left.\{-(\lambda-1)R\}-S\ln\left(\frac{\lambda+1}{\lambda-1}\right)\right]-3S\lambda e^{-\lambda R/2}\Big\}d\lambda.$$

E. C. KEMBLE
F. F. RIEKE
Jefferson Physical Laboratory,
Harvard University,
June 11, 1930.

BOOK REVIEWS

Physique Moderne. GAETANO CASTELFRANCHI, (Translation from the Italian by M. A. Quemper de Lanascol), 2+660 pp., 147 figures, Albert Blanchard, Paris, 1930, Price 70 francs.

This is a summary of modern physics, written for the educated layman and for the scientist whose work lies outside the field of physics, rather than for the physicist or for the student of physics. For the most part, the mathematics is subordinated to such a degree that a person who has, or who once had, a slight acquaintance with the calculus, will be able to follow the treatment. The book differs somewhat in subject matter from volumes in English which have a similar purpose. An introductory chapter deals with history and with the most elementary facts in regard to atoms and molecules. There is a chapter on the classical theory of light and one which reviews the kinetic theory of gases from an elementary standpoint. Chapters IV and V on the Brownian movement and fluctuation phenomena are entertaining and give considerable insight into the physics underlying the statistical equations which govern these subjects. There are conventional chapters on special relativity and on electrons and positive rays. Then we have a discussion of x-rays, the determination of atomic numbers with their aid, and the structure of crystals. A chapter on radioactivity introduces the nuclear atom, which is first discussed from the standpoint of Rutherford's early scattering experiments. The concept of quanta is introduced via the black-body-radiation route. Bohr's theory of hydrogen is treated much as it is in any elementary English book on atomic structure. Chapter XIV develops the elements of generalized dynamics and applies them to the Zeeman and Stark effects. In the same chapter, we find a very brief account of line and band spectra and of Pauli's principle. Then we encounter specific heats, photoelectric effects (including a brief section on the experiments of Auger), the Compton effect, and other experiments on the structure of radiation. The treatment of magnetism is quite pleasing.

As the author says, his discussion of wave mechanics follows closely that of Darrow, published in the "Bell System Technical Journal" for 1927. The author's decision to do this is commendable, for the reviewer knows of no clearer treatment than that in Darrow's article. The principal application of wave mechanics given in this chapter is that of electron diffraction. The discussion of experiments on this subject is well written. The book ends with a chapter on the new statistics.

No doubt this book will be well received by persons who speak the Romance languages. Its subject matter is already well covered in English by a variety of entertaining and well written books, such as those of Darrow, Andrade, and Haas. The treatment is superficial and the book is not to be recommended as mental food for the serious student of physics. However, this criticism must not be interpreted severely, for the reviewer believes that the volume is well suited to the class of readers for whom it was obviously intended.

ARTHUR E. RUARK

Essai sur les Principes de la Thermodynamique. I.-N. LONGINESCU, with a preface by A. Boutaric, 80 pp., 13×20 cm. Société d'Éditions Scientifiques, Paris, 1929.

In this essay an attempt is made to embrace under the same broad point of view the First and Second Laws of Thermodynamics and the Principle of Least Action. This is done by a quasi-logical deduction from certain general philosophical considerations, among which the notion of causality is important. I do not suppose, however, that even the author would claim that this deduction has any binding logical force, or that more has been achieved than to show in a suggestive way that the notions of thermodynamics fit consistently into a broader sort of physical outlook. The work as a whole may be described as a pleasantly sophisticated essay, which the physicist already familiar with thermodynamics may read with a certain satisfaction, but which is not intended for the beginner or for the physicist who is seriously interested in resolving the logical difficulties in thermodynamics emphasized by recent developments.

P. W. BRIDGMAN

Radio Technic. VI. Die electrischen Wellen. F. KIEBITZ. Pp. 125, 28 figs. Walter de Gruyter and Co., Berlin. Price RM 1.50.

This is a thin book of pocket size, the sixth of a series dealing with radio practice each by a different author and appearing under the general classification of "Sammlung Göschen." The booklet under review is concerned with an elementary exposition of the nature, propagation and reflection of electromagnetic waves and their radiation and reception by practical antennas and antenna systems.

The treatment is brief and in general takes the form of stating the equations of interest and considering their numerical application to commonly encountered oscillation circuits and radio antennas. The author usually gives the range through which a quantity under consideration may be expected to vary in practice. Although elementary, the treatment is sound and accurate, qualities not found in a great deal of the literature on radio recently appearing.

H. E. HARTIG

Die Grundgedanken der neueren Quantentheorie. O. HALPERN AND H. THIRRING. Pp. 241. J. Springer, Berlin, 1929.

This article is a separate issue from volume 8 of the annual "Ergebnisse der Exakten Naturwissenschaften." There are four chapters: Relativity and electron spin, One body problems, Many body problems, and Interpretation of the theory. The first chapter includes an account of the Dirac electron theory. The second treats a wide variety of problems, oscillator, rotator, hydrogen atom, radioactivity, dispersion and Compton effect, in a concise and simple manner. The third discusses symmetry of the eigenfunctions and simple applications to the helium atom, to band spectra, and gives an account of the new statistics. The last chapter gives an unusually clear account of the statistical interpretation and the uncertainty relation.

E. U. CONDON.

The Conduction of Electricity through Gases. K. G. EMELÉUS. Pp. X+94, 37 figures. E. P. Dutton and Co. Inc., New York City. Price $1.10.

This book is one of a series of small monographs on physical subjects, edited by B. L. Worsnop. The author confines himself to a treatment of electrical discharges at low gas pressures. He condenses into a few small pages a great deal of information regarding the complex phenomena involved, and points out and briefly discusses some of the outstanding problems of the subject. A chapter is devoted to exploring electrodes.

JOHN ZELENY